THERMAL DECOMPOSITION REACTIONS OF ORGANIC SULFONYL AZIDES

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Submitted to the Faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May 29, 1960

THERMAL DECOMPOSITION REACTIONS OF

ORGANIC SULFONYL AZIDES

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ACKNOWLEDGEMENT

The author wishes to express his thanks to Dr. Marvin T. Edmison for his guidance, helpful criticism and counsel, which have made the experimental work and preparation of this disseration possible and much more pleasant.

The author also wishes to express his appreciation to Dr. O. C. Dermer for his suggestions and guidance throughout this investigation and to Dr. George Gorin for his suggestions and help with the kinetic studies.

The author also wishes to express his sincere gratitude to his wife, Louise, whose patience, understanding and moral support have made working toward this degree more enjoyable.

Acknowledgement is also made for the financial support furnished by a Research Assistantship received through the Research Foundation and supported by a contract with Wright Air Development Center of the U.S. Air Force.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	3
Organic Azides	3
Structure	3
Preparation	5
Chemical Properties	5
Kinetic Studies	8
EXPERIMENTAL	10
Preparation of Reagents	10
Preparation of 1,4-Benzenedisulfonyl Azide	10
Preparation of 1,3-Benzenedisulfonyl Azide	10
Comparison of Nitrogen Analyses	14
Preparation of 4,4'-Biphenyldisulfonyl Azide	15
Preparation of 1,5-Naphthalenedisulfonyl Azide	16
Preparation of Benzenesulfonyl Azide and Methanesulfonyl Azide	17
Preparation of 4-Nitrobenzenesulfonyl Azide	18
Thermal Decomposition of Aromatic Sulfonyl Azides and Analyses of Products	19
Thermal Decomposition of 1,4-Benzenedisulfonyl Azide in Organic Substrates	19
Isolation of Sulfonamides	20
Preparation of Comparison Standards for the Reaction of 1,4-Benzenedisulfonyl Azide with Biphenyl and with Toluene	22
Methyl Cellosolve Extraction	27
Attempt at Further Substitution	28
Thermal Decomposition of 1,4-Benzenedisulfonyl Azide Alone	30
Gas Collections from 1,4-Benzenedisulfonyl Azide	33
Results of Gas Collections from 1,4-Benzenedisulfonyl Azide	33
Thermal Decompositions of 1,3-Benzenedisulfonyl Azide	35
Results of Gas Collections from 1,3-Benzenedisulfonyl Azide	39
Thermal Decompositions of 4,4'-Biphenyldisulfonyl Azide and 1,5-Naphthalenedisulfonyl Azide	41
Results of Gas Collections From 4,4'-Biphenyldisulfonyl Azide	45
Decompositions of other Aromatic Azides	45

Page

Thermal Decomposition of Methanesulfonyl Azide 47
Products of Decomposition of Methanesulfonyl Azide in in Xylene 47
Products of Decomposition of Methanesulfonyl Azide Alone. 50
Kinetic Studies of the Decomposition of Methanesulfonyl Azide in Xylene 53

DISCUSSION AND CONCLUSION

Products of Thermal Decompositions of 1,4-Benzenedisulfonyl Azide 60
Proposed Mechanism of Reaction at Lower Concentrations of Aromatic Disulfonyl Azide 63
Proposed Mechanism of Reaction for Organic Sulfonyl Azides Decomposed Alone 63
Intermediate obtained from the Thermal Decomposition of 1,4-Benzenedisulfonyl Azide Alone. 65
Interpretations from Amount of Gas Collected 66
Comparison of 1,3-Benzenedisulfonyl Azide with 1,4-Benzenedisulfonyl Azide 67
Comments about the 4,4'-Biphenyldisulfonyl Azide 69
Products of Thermal Decomposition and Proposed Mechanism of Reaction at low concentrations of Methanesulfonyl Azide . . . 70
Kinetic Studies of Methanesulfonyl Azide Decomposed in Xylene . 71

SUMMARY 74

SUGGESTIONS FOR FUTURE WORK 77

BIBLIOGRAPHY 78

LIST OF TABLES

Table		Page
I.	Nitrogen Analyses of 1,4-Benzenedisulfonyl Azide	16
II.	Nitrogen Analyses of 1,3-Benzenedisulfonyl Azide	16
III.	Summary of Melting Points of Compounds Prepared	19
IV.	Thermal Decomposition Concentrations of 1,4-Benzenedisulfonyl Azide	20
V.	Gas Collected From Thermal Decompositions of 1,4-Benzenedisulfonyl Azide in Biphenyl Substrate and Alone	34
VI.	Thermal Decomposition Concentrations of 1,3-Benzenedisulfonyl Azide	35
VII.	Gas Collected From Thermal Decompositions of 1,3-Benzenedisulfonyl Azide in Biphenyl Substrate and Alone	41
VIII.	Thermal Decomposition Concentrations 4,4'-Biphenyldisulfonyl Azide and Thermal Decomposition Concentrations of 1,5-Naphthalenedisulfonyl Azide.	44
IX.	Gas Collected From Thermal Decomposition of 4,4'-Biphenyldisulfonyl Azide in Biphenyl Substrate and Alone	47
X.	Thermal Decomposition of Methanesulfonyl Azide in Xylene	49
XI.	Gas Collected from Thermal Decomposition of Methanesulfonyl Azide in Xylene during Eleven Hours	56
XII.	Gas Collected From Thermal Decomposition of Methanesulfonyl Azide in Xylene During Forth-Eight Hours	57
XIII.	Rate Constants for the Thermal Decompositions of Methanesulfonyl Azide in Xylene	72

LIST OF FIGURES

Figure — Page

1. Absorption Curves of Mineral Oil, Polymer Made From 1,4-Benzenedisulfonyl Chloride and Benzidine With Pyridine, and N,N-Dimethyl Aniline, as Hydrogen Chloride Acceptors. . . 23

2. Absorption Curves of the Products from Decomposition of 1,4-Benzenedisulfonyl Azide in Biphenyl at Azide Concentration of 3.8, 20, 30, and 40 Mole Per Cent 24

3. Absorption Curves for the Polymer prepared from 1,4-Benzenedisulfonyl Chloride and Benzidine and the Product from Decomposition of 40 Mole Per Cent 1,4-Benzenedisulfonyl Azide in Biphenyl 25

4. Absorption Curves of a One to One Mixture of N,N'-bis(Biphenylyl)-1,4Benzenedisulfonamide and N,N'-bis(2-Biphenylyl) 1,4-Benzenedisulfonamide and The Product from Decomposition of 40 mole Per Cent 1,4-Benzenedisulfonyl Azide in Biphenyl . 26

5. Absorption Curves of Potassium 1,4-Benzenedisulfonate and the Product from 1,4-Benzenedisulfonyl Azide Decomposed Alone . . 32

6. Absorption Curves of the Product from the Decomposition of 1,3-Benzenedisulfonyl Azide in Biphenyl at Azide Concentrations of 5.0, 9.7, 17.5 and 29.8 Mole Per Cent 36

7. Absorption Curves of the Product from Decomposition of 17.5 Mole Per Cent 1,3-Benzenedisulfonyl Azide in Biphenyl and a One to One Mixture of N,N'-bis(2-Biphenylyl)-1,3-Benzenedisulfonamide and N,N'-bis(4-Biphenylyl)-1,3-Benzenedisulfonamide 38

8. Absorption Curves of the Product from 1,3-Benzenedisulfonyl Azide Decomposed Alone and Sodium 1,3-Benzenedisulfonate . . 40

9. Absorption Curves of the Product from the Decomposition of 4,4'-Biphenyldisulfonyl Azide in Biphenyl at Azide Concentrations of 5.0, 9.7, 17.5 and 29.8 Mole Per Cent 42

Figure Page

10. Absorption Curves of the Product from the Decomposition of 5.0 Mole Per Cent 4,4'-Biphenyldisulfonyl Azide in Biphenyl and a One to One Mixture of N,N'-bis(2-Biphenylyl)-4,4'-Biphenyldisulfonamide and N,N'-bis(4-Biphenylyl)-Biphenyldisulfonamide 43

11. Absorption Curves of the Product from 4,4'-Biphenyldisulfonyl Azide Decomposed Alone and Sodium 4,4'-Biphenyldisulfonate . 46

12. Absorption Curves of the Product from Decomposition of Methanesulfonyl Azide in Xylene at Azide Concentrations of 4.8, 10.1 19.2 and 28.9 Mole Per Cent 51

13. Absorption Curves of N-(para-Xylyl)Methanesulfonamide and the Product from Decomposition of 10.1 Mole Per Cent Methanesulfonyl Azide in Xylene. 52

14. Absorption Curves of the Product from Methanesulfonyl Azide Decomposed Alone and of Sodium Methanesulfonate 54

15. Ml. of Nitrogen Evolved from the Decomposition of Methanesulfonyl Azide in Xylene versus Time in Hours 58

16. Ml. of Nitrogen Evolved from the Decomposition of Methanesulfonyl Azide in Xylene versus Time in Hours 59

INTRODUCTION

Modern aircraft are able to fly so fast that heat is generated due to friction with the air. This has created many problems, among which is the need for a pliable organic material that can be molded and yet withstand high temperature. It is common knowledge that sulfonamides are relatively high-melting organic compounds. With this in mind, this experimentation was undertaken to see how large a molecule containing repeating sulfonamide linkages could be made by thermally decomposing aromatic sulfonyl azides.

When a sulfonyl azide is heated, it decomposes to give off nitrogen and form a radical. This radical is capable of combining with other substances, e.g., it will attack an aromatic nucleus to form a sulfonamide. If a compound containing two sulfonyl azide groups is heated it should be possible to produce a compound with repeating sulfonamide linkages. This research consisted of an investigation of the reaction when sulfonyl azides were thermally decomposed alone and in the presence of other compounds.

Aromatic disulfonyl azides were prepared by converting aromatic disulfonic acids to the aromatic disulfonyl chlorides and these to the aromatic disulfonyl azides. The aliphatic sulfonyl azide was prepared from the aliphatic sulfonyl chloride.

The azides used in this research were 1,3-benzenedisulfonyl azide, 1,4-benzenedisulfonyl azide, 1,5-naphthalenedisulfonyl azide, 4,4'-

biphenyldisulfonyl azide and methanesulfonyl azide. These azides were decomposed separately in toluene, xylene, naphthalene, biphenyl, *para*-dichlorobenzene and 1,2,4,5-tetrachlorobenzene as individual substrates.

At first, the decomposition in a particular substrate was carried out with an azide concentration of approximately 5 mole per cent; the concentration then was raised stepwise in individual experiments until it was approximately 35 mole per cent.

It soon became evident that molecules containing many sulfonamide linkages were not being made by this method. One of the bases for this conclusion was the fact that reaction mixtures containing high concentration of azide gave off so much nitrogen that the formation of a large number of sulfonamide linkages could not have occurred. By collecting the gas which was evolved from a reaction, it was possible to estimate the amount of nitrogen that could be available for sulfonamide formation.

The final objective of this thesis was to make a study of the reaction in as much detail as possible to try to understand what actually occurs. It appears that such a study has not been done by other investigators and the results should be useful to future workers in this area of research; in fact, it was hoped that such a study might point the way to the attainment of our original objective. Accordingly, some kinetic studies have been made, reaction products have been identified where possible, and a possible mechanism has been postulated.

HISTORICAL

Several discussions of organic azides have appeared in the literature in recent years (17, 28, 31, 38, 51, 53) including a comprehensive review by Boyer and Canter (12). The following historical section is intended only to include material pertinent to this dissertation and to summarize the more recent literature.

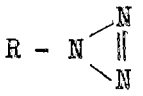
The author is indebted to Boyer and Canter (12) and to Heacock (38) for their reviews of organic azides. A considerable portion of the work reviewed here was presented in their reviews.

ORGANIC AZIDES

Structure

The azide group has attracted attention since the discovery of phenyl azide (37) in 1864 and of hydrogen azide (20) in 1890.

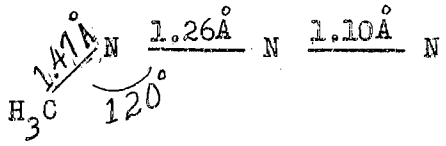
The first structural formula was proposed by Fischer (33) in 1877 and supported by Curtius (26) in 1891. It was a cyclic structure of three nitrogen atoms.



The presently accepted structure of the azide ion was established by Hendricks and Pauling (39) using X-ray analysis of sodium and potassium azides.

Bragg (13), Hughes (41), Knaggs (41, 42) and Sutton (55) by X-ray analysis of cyanuric triazide, found the same structure for the azide ion. Langseth and Nielsen, (43) using Raman spectra of the ion in solution, supported the x-ray analyses. The ion has the structure, $[\ddot{N}::N::\ddot{N}]^-$, with the nitrogen atoms lying in a straight line. However, a satisfactory covalently bonded linear formula could not be written that would satisfy all chemical and physical properties. A covalently bonded molecule would have structures such as $R-\dot{N}=\overset{+}{N}=\overset{-}{N}$ or $R-\overset{-}{N}-\overset{+}{N}\equiv N$. Either structure would require a considerable dipole moment. Since phenyl azide has a moment of only 1.55 (52) a resonance hybrid has been suggested (8, 36, 44, 54) in which the two classical structures shown above are the main contributing isomers. Thus the low dipole moment is explained since the two dipoles are in opposite directions and nearly equal.

Brockway and Pauling (14, 45) used electron diffration to determine the interatomic distances in methyl azide and found the following structure:



These bond distances between the nitrogen atoms calculated by the electron diffraction method as 1.26 Å and 1.10 Å, and are in close agreement with 1.25 Å and 1.12 Å, which are the values obtained by the molecular orbital method (10), and with 1.22 and 1.10 Å which were obtained from considerations of dipole moment data (48). Interpretations of electron difraction studies suggested a C - N - N bond angle of 120°, in agreement with interpretation of absorption spectra (9).

Calculations according to the method of molecular orbitals indicated that in covalent azides, e.g., methyl azide, the nitrogen atoms have

charges of -0.37, 0.52 and -0.15, respectively (10).

Experimental evidence for a linear structure in phenyl azide was obtained by Clusius and Weisser (18). They prepared phenyl azide containing terminal N^{15}, from phenylhydrazine and nitrous acid containing N^{15}. A study of the reduction products of the 1,3-diphenyltriazene obtained from the azide and phenylmagnesium bromide, was in agreement with the linear structrue. These results were confirmed by Clusius and Hurzeler (19).

Preparation

Organic azides are usually prepared by direct displacement of another group by the azide ion, or by stepwise introduction of the three nitrogen atoms.

Ever since Curtius obtained benzyl azide from benzyl iodide and silver azide (23) the direct displacement method has proved to be of general usefulness and not only halogens, but sulfate, nitro, phenylazo, hydroxyl, nitrate, iodoxy and alkoxy groups also have been found to be displaced by the use of a metallic azide or hydrogen azide (12, 38).

The stepwise method is usually not a practical method for the preparation of acyl and aryl azides.

Sulfonyl azides have been prepared by the displacement method and by the nitrosation of a hydrazide (22).

Chemical Properties

Azides, in general, are oily liquids or low-melting solids that decompose slowly if heated gradually, but explode violently on rapid

heating. The reactions of the azides are conveniently arranged into three main classes: displacement, decomposition, and addition reactions. These reactions are thoroughly discussed by Boyer and Canter (12) so only the more pertinent are reviewed here.

The azides have been decomposed thermally without catalysts, and also by acid and by base catalysis. These decompositions take place with the formation of a multitude of products. Curtius (21, 23, 24, 25) postulated that four different reactions occur simultaneously in the acid-catalyzed decomposition of alkyl azides.

A. $RCH_2N_3 \longrightarrow RCH{:}NH + H_2C{:}NR + N_2$

B. $RCH_2N_3 \longrightarrow RCH_2NH_2 + N_2$

C. $RCH_2N_3 \longrightarrow RCH{:} + HN_3$

$RCH{:} + RCH_2N{:} \longrightarrow RCH{:}NCH_2R$

D. $RCH_2N_3 + H_2O \longrightarrow RCH_2OH + HN_3$

Later work by Sherk, Houpt, and Brown (49) established that reaction "A" predominates.

Bamberger and his pupils (5, 6, 7) made a concentrated study of the decomposition of p-tolyl azide in aqueous sulfuric acid and found the reaction products to include amines, aminophenols and unidentified amorphous acids and bases. After carrying out this reaction at -20°C., they were successful in isolating a low-molecular-weight polymer, which Bamberger considered to contain a repeating quinonoid structure. Methyl and ethyl azides (51) in the gas phase undergo a homogeneous unimolecular pyrolysis at a measurable rate to produce ethylene. Ethyl azide also shows nitrogen-nitrogen splitting and produces a mixture of amines as well as ethylene.

The aryl azides are usually more stable, although they decompose slowly between 150°-200°C. Substitution in the ortho position usually decreases the azide stability. o-Nitrophenyl azide liberates nitrogen at temperatures as low as 85°C. The aryl azides are apparently unable to rearrange, and most of their reactions seem to have a biradical as an intermediate. This radical apparently is able to abstract hydrogen from the solvent to form an arylamine, or to dimerize to form an azobenzene derivative (51).

The acyl azides decompose thermally to give the Curtius rearrangement as shown below:

$$RCON_3 \longrightarrow RCON: \longrightarrow RNCO + N_2$$

The details of the mechanism of the rearrangement have not been determined, but it is fairly well accepted that nitrogen is expelled with the formation of the biradical intermediate. An excellent review of the Curtius rearrangement was written by Peter A. S. Smith (53).

The rigid azides, such as the sulfonyl azides, the diazides of carbonic acid and the azides of sulfuric, carbamic and phenylcarbamic acids, fail to undergo rearrangement, but the biradical which is formed either couples or extracts hydrogen from an aromatic solvent (46, 51).

Curtius and co-workers (22), Dermer and Edmison (29, 31), and Heacock (38) have studied the products obtained from the decomposition of aromatic sulfonyl azides in the presence of aromatic solvents. The reaction can be conceived as follows (30):

A. $ArSO_2N_3 \longrightarrow ArSO_2N: + N_2$

B. $ArSO_2N: + Ar'H \longrightarrow ArSO_2NHAr'$

Curtius and co-workers (22) also have studied the products obtained from the decomposition of aromatic disulfonyl azides in the presence of aromatic solvents. In all their experiments they isolated the N-substituted disulfonamides.

Ring attack does not always take place when aromatic sulfonyl azides are decomposed in aromatic solvents as was shown by Buchanan and Levine (15). The structure of the compounds form when aromatic sulfonyl azides are decomposed in pyridine is that of a quaternary salt, $C_5H_5\bar{N}\text{-}\overset{+}{N}\text{-}SO_2Ar$ (12). Datta (27) substantiated this work.

Decomposition of aromatic sulfonyl azides in the presence of either nitrobenzene and benzaldehyde, respectively, fails to give the substituted products, but nitric oxide was observed as a by-product in the attempted substitution of nitrobenzene (29).

Kinetic Studies

There was very little literature found on kinetics of the decomposition of organic azides, and no literature precedence was found of a kinetic study of the decomposition of an organic sulfonyl azide.

Audubert (3) in 1937 irradiated sodium and potassium azides with ultraviolet light and found the rate of decomposition to be proportional to the intensity of radiation.

In 1942, Bonnemay (11) experimented with solutions of the alkaline azides under the influence of ultravoilet rays. He followed the progress of the reaction by the change of pH of the solution. The longer the azide was irradiated the higher the pH of the resulting solution, until a maximum of 11.8 was reached.

Organic azides were decomposed for kinetic studies by Yoffe (57) in 1951. He experimented with trinitrotriazidobenzene and cyanuric triazide. They were thermally decomposed and the nitrogen was collected, but the rate of decomposition was so fast that rate constants could not be calculated.

In 1955, Russell (47) decomposed phenyl azide at 130°C., at concentrations of 0.03 to 0.3 mole/liter separately in tetrahydronaphthalene and nitrobenzene. He found the reaction to be first order in both solvents.

An excellent kinetic study of the thermal decomposition of o-nitrophenyl azide was made by Fagley and Co-workers (32) when they studied the decomposition in di-n-butyl phthalate, cyclohexanol, n-heptane and mixtures of cyclohexanol and heptane over a temperature range of 68° to 90°C. They found first order kinetics for the decomposition and rate constants were calculated.

EXPERIMENTAL

Reagents used in the experimental work for this dissertation were C.P.-grade, if they were commercially available. In cases where C.P.-grade reagents were not available, the purest starting material obtainable was used. Solids were purified further by recrystallization and liquids were purified further by distillation as needed.

PREPARATION OF REAGENTS

Preparation of 1,4-Benzenedisulfonyl Azide

Since 1,4-benzenedisulfonyl azide was not found in the literature, a detailed procedure for its preparation is given. The method for preparing the 1,4-benzenedisulfonic acid is essentially that of Wynne and Bruce (56) for the preparation of toluene-3,4-disulfonic acid. The conversion to the 1,4-benzenedisulfonyl chloride was by a variation of the method for converting 1,5-naphthalenedisulfonic acid to the naphthalenedisulfonyl chloride as described in Organic Synthesis (16). The conversion of the 1,4-benzenedisulfonyl chloride to the 1,4-benzenedisulfonyl azide was accomplished by a variation of the method used by Edmison (31) and later by Heacock (38) for the conversion of benzenesulfonyl chloride to benzenesulfonyl azide.

Eighty grams of sulfanilic acid were added to 100 ml. of water and the mixture cooled to 0°C. in an ice bath. Forty grams of sodium nitrite were added, in 2-gram portions, over a period of two hours with stirring.

This was done in a hood. The gray sulfanilic acid turned to a deep brown color. Fifty millileters of concentrated hydrochloric acid were added and a yellow diazo-compound settled on standing and the mother liquor was decanted off. This compound was then washed with ice water and filtered. The diazo-compound is relatively stable at room temperature although it decomposes on prolonged standing or exposure to sunlight. The diazo-compound was made into a paste by the addition of a small amount of water.

Potassium ethylxanthate, used in the next step, was prepared by dissolving 56 grams of potassium hydroxide in 150 grams of ethyl alcohol. Eighty milliliters of carbon disulfide were added and the solution was evaporated to obtain the potassium ethylxanthate.

A solution containing 70 grams of potassium ethylxanthate in 700 ml. of water was heated to 60°C., in a hood, and stirred rapidly by means of a mechanical stirrer. The diazo-compound paste was added to this solution in one half to one gram increments. A vigorous reaction took place after each addition with very much foaming and effervescence which subsided rapidly. This foaming was due to the release of nitrogen and carbon oxysulfide during the formation of potassium 4-(ethylthio)benzenesulfonate. The 4-(ethylthio)benzenesulfonate was converted to potassium benzene-disulfide-4,4'-disulfonate by air oxidation. The potassium benzenedisulfide-4,4'-disulfonate was dissoloved in 150 ml. of water and poured, with rapid stirring, into 800 ml. of alcohol. This precipitated the desired compound while an orange-red by-product remained dissolved in the alcohol. The potassium salt was filtered off and dried 24 hours at room temperature to remove the alcohol. When dry, it was added to 1000 ml. of water.

Approximately 50 grams of potassium permanganate were needed to oxidize the potassium benzenedisulfide-4,4'-disulfonate to the potassium 1,4-benzenedisulfonate. The permanganate was added to the stirred solution at 70°C. until a pink color persisted for 15 minutes. The excess permanganate was destroyed by adding ethyl alcohol. The solution was cooled, to allow the manganese dioxide to settle, and was filtered with suction through Whatman No. 3 very retentive filter paper. The manganese dioxide that was retained on the filter was then extracted with 500 ml. of hot water, to remove more of the potassium 1,4-benzenedisulfonate. Combining and evaporating the filtrates left the potassium salt of 1,4-benzenedisulfonic acid. The yields varied from 47.3 to 49.7 per cent based on sulfanilic acid.

Fifty grams of the potassium 1,4-benzenedisulfonate were mixed dry with 80 grams of phosphorus pentachloride in a hood. This mixture was placed in a one-liter three-neck distilling flask fitted with an air condenser which was connected to a calcium chloride drying tube. The flask was placed in an oil bath at 140°C. and heated for four hours with periodic stirring. The flask was then cooled and the phosphorus oxychloride was distilled off under vacuum from a water aspirator. Five hundred milliliters of chloroform were added to the solid mass and then 250 ml. of water were added to dissolve the water-soluble products and the unreacted reagents. The phases were separated in a separatory funnel and most of the chloroform was distilled off from the nonaqueous phase. When the volume had been cut to approximately 50 ml., distillation was stopped and the liquid was poured on ice to precipitate the 1,4-benzenedisulfonyl chloride. This was then recrystallized from chloroform. The

melting point was 138°C. as compared to literature values of 138° and 139°C. Yields based on the dipotassium salt were 75 to 89 per cent.

The final step was conversion to 1,4-benzenedisulfonyl azide. Twenty-seven and one-half grams of the 1,4-benzenedisulfonyl chloride were dissolved in 100 ml. of acetone and 21 grams of sodium azide were dissolved in 50 ml. of water. The azide solution was stirred with a mechanical stirrer and the acetone solution was added dropwise over a period of one hour. Stirring was continued for two more hours after addition of the 1,4-benzenedisulfonyl chloride was completed. Care had to be taken that the temperature did not rise too rapidly. Two hundred and fifty milliliters of water were added to precipitate the 1,4-benzenedisulfonyl azide and stirring was continued for another 30 minutes. The azide was then filtered off and recrystallized two times from ethyl alcohol. The solubility of this azide in alcohol is about five grams per 100 ml. of alcohol at 70°C. The azide appeared as needles and is a fluffy white powder when dry, with a melting point of 137°-138°C. Yields of 1,4-benzenedisulfonyl azide ranged from 90 - 96 per cent based on the dichloride.

The 1,4-benzenedisulfonyl azide was analyzed by Geller Microanalytical Laboratories in New York for total nitrogen and for the amount of nitrogen released at 120°C. For duplicate analyses they reported 28.91 and 28.87 per cent total nitrogen. The theoretical value for nitrogen is 29.16 per cent. The amount released on heating to 120°C. was 23.64 and 23.91 per cent. This is just slightly smaller than the amount the author found which is reported later in this dissertation.

Confirmation of the identity of the 1,4-benzenedisulfonyl chloride was obtained by preparing 1,4-benzenedisulfonamide. Two grams of the 1,4-benzenedisulfonyl chloride were suspended in 25 ml. of concentrated ammonium hydroxide and heated for two hours. The solution was cooled and acidified with hydrochloric acid to precipitate the 1,4-benzenedisulfonamide. It was filtered off and recrystallized from water. When dry, the melting point was 287°C. as compared to a literature value of 288°C.

Preparation of 1,3-Benzenedisulfonyl Azide

1,3-Benzenedisulfonyl azide was prepared by the method used in preparing 1,4-benzenedisulfonyl azide. Since 1,3-benzenedisulfonic acid is commercially available, the procedure was shortened considerably. The acid was neutralized with two moles of sodium hydroxide to give the sodium salt. This was dried and treated with phosphorus pentachloride to give 1,3-benzenedisulfonyl chloride. The melting point was 62°C. as compared to a literature value of 63°C. The 1,3-benzenedisulfonyl chloride was converted to 1,3-benzenedisulfonyl azide by reaction with sodium azide as previously described for the 1,4-isomer. The melting point was 83° - 84°C. as compared to the literature value of 82°C. Yields were similar to those obtained in the preparation of 1,4-benzenedisulfonyl azide.

The 1,3-benzenedisulfonyl azide was also analyzed by Geller Laboratories for total nitrogen and for the amount of nitrogen released at 120°C. For duplicate analyses, they reported 29.08 and 29.18 per cent total nitrogen. Theoretical nitrogen is 29.16 per cent. The amount released on heating to

120°C. was 25.69 and 25.86 per cent which is slightly smaller than the amount found by the author.

The 1,3-benzenedisulfonyl chloride was also converted to 1,3-benzenedisulfonamide by the procedure previously described for the conversion of 1,4-benzenedisulfonyl chloride to the 1,4-benzenedisulfonamide. The melting point was 229°C. as compared to a literature value of 229°C.

Comparison of Nitrogen Analyses

The 1,4-benzenedisulfonyl azide and 1,3-benzenedisulfonyl azide used in the experimentation were at least 99 per cent pure. This is based on the total amount of nitrogen found in these compounds. In Tables I and II the amount of nitrogen found in .006937 mole of these azides, by Geller Microanalytical Laboratories and by the author, are compared. The labile nitrogen is considered as the nitrogen which was evolved by heating the azides at 120°C. until no more nitrogen was evolved. Analyses of residual nitrogen were made on the same samples, after all the labile nitrogen had been evolved. Geller also analysed for total nitrogen in the compound. These values were identical with the ones reported in the tables, but were from different samples.

The total nitrogen evolved is very close to the theoretical amount of nitrogen that should be present. However, there is a variation within an analysis as high as $\pm$ 4 per cent. Part of this error should be due to incomplete analysis of labile nitrogen. This nitrogen would thus appear as residual nitrogen.

TABLE I

NITROGEN ANALYSES OF 1,4-BENZENEDISULFONYL AZIDE
(BASED ON .006937 MOLE OF SAMPLE)

Analyst[1]	Labile N_2 ml. S.T.P.	Average	Residual N_2 ml. S.T.P.	Average	Total	Theoretical
G	378		84			
G	382	380	78	81	461	466
A	386		71			
A	388	387	73	72	459	466

1/ G, Geller Laboratory; A, Author

TABLE II

NITROGEN ANALYSES OF 1,3-BENZENEDISULFONYL AZIDE
(BASED ON .006937 MOLE OF SAMPLE)

Analyst[1]	Labile N_2 ml. S.T.P.	Average	Residual N_2 ml. S.T.P.	Average	Total	Theoretical
G	411		56			
G	413	412	52	54	466	466
A	414		52			
A	420	417	48	50	467	466

1/ G, Geller Laboratory; A, Author

Preparation of 4,4'-Biphenyldisulfonyl Azide

The 4,4'-biphenyldisulfonyl azide was prepared from commercially available 4,4'-biphenyldisulfonic acid. The acid was neutralized with sodium hydroxide and converted to the sulfonyl chloride by reaction with phosphorus pentachloride. The 4,4'-biphenyldisulfonyl chloride was found

to be almost insoluble in chloroform. However, it was obtained in a relatively pure state by triturating with hot water. Extreme care must be exercised when adding water to the anhydrous reaction products in the flask. If too much water is added at one time, the reaction is very vigorous. Although the solubility is limited 4,4'-biphenyldisulfonyl chloride was purified by recrystallization from ethyl alcohol. The melting point was 206° - 207°C. as compared to a literature value of 206°C. This chloride is practically insoluble in acetone, but reaction with sodium azide was accomplished by rapidly stirring the solution while adding the sodium azide. The azide was isolated and purified by methods described for the 1,4-benzenedisulfonyl azide. The melting point was 144.5° - 145°C. compared to a literature value of 144° - 145°C.

Preparation of 1,5-Naphthalenedisulfonyl Azide

The sodium 1,5-naphthalenedisulfonate is commercially available, and from this, the 1,5-naphthalenedisulfonyl azide was prepared in a manner analogous to the preparation of 4,4'-biphenyldisulfonyl azide previously described. The melting point of 1,5-naphthalenedisulfonyl chloride was 181°C. compared to a literature value of 183°C. The melting point of 1,5-naphthalenedisulfonyl azide was 175° - 176°C. as compared to a literature value of 177°C.

Preparation of Benzenesulfonyl Azide and Methanesulfonyl Azide

Benzenesulfonyl azide was prepared by the method of Edmison (31) and Heacock (38). In this method, sodium azide was dissolved in twice its weight of water. To this solution was added twice its volume of

95 per cent alcohol. Benzenesulfonyl chloride, diluted with twice its volume of 95 per cent alcohol, was slowly added with mechanical stirring to the cold sodium azide solution. After the addition, stirring was continued for one hour. The solution was transferred to a separatory funnel and an equal volume of water was added. Upon standing a clear colorless oil separated at the bottom. The water layer was twice extracted with one-fifth its volume of ethyl ether, and the extract was added to the oil in a separatory funnel. The ether solution was then washed four times with one-half its volume of water each time, after which the ether layer was separated and dried with anhydrous sodium sulfate. The ether was removed by warming on a water bath at 50°C. under vacuum from a water aspirator.

This method was also used for the preparation of methanesulfonyl azide.

Preparation of 4-Nitrobenzenesulfonyl Azide

Commercially available 4-nitrobenzenesulfonyl chloride was treated with sodium azide to convert it to the 4-nitrobenzenesulfonyl azide. The melting point is 100°C. This compound has not previously been reported in the literature.

A summary of the melting points of the compounds prepared is shown in Table III.

TABLE III

SUMMARY OF MELTING POINTS
OF COMPOUNDS PREPARED

Compounds	m.p. °C.	Lit. m.p. °C.
1,4-benzenedisulfonyl chloride	138	138 - 139
1,4-benzenedisulfonyl azide	137	---
1,4-benzenedisulfonamide	287	288
1,3-benzenedisulfonyl chloride	62	63
1,3-benzenedisulfonyl azide	83-84	82
1,3-benzenedisulfonamide	229	229
4,4'-biphenyldisulfonyl chloride	206-207	206
4,4'-biphenyldisulfonyl azide	144.5 - 145	144-145
1,5-naphthalenedisulfonyl chloride	181	183
1,5-naphthalenedisulfonyl azide	175 - 176	177
4-nitrobenzenesulfonyl azide	100	---

THERMAL DECOMPOSITIONS OF AROMATIC SULFONYL AZIDES AND ANALYSES OF PRODUCTS

Thermal Decomposition of 1,4-Benzenedisulfonyl Azide in Organic Substrates

With few exceptions, the decompositions were carried out at 120°C. using a wax bath for uniform heating. A few experiments were run in an attempt to find a solvent that would boil high enough and would not be attacked by the azide when it decomposed. Such an inert solvent was not found.

Aromatic substrates which were selected to react with the azide were toluene, xylene, biphenyl, naphthalene, 1,4-dichlorobenzene and 1,2,4,5-tetrachlorobenzene. A summary of the compositions of these mixtures are given in Table IV below. They are reported in mole ratios. The reaction of toluene with 1,4-benzenedisulfonyl azide is the only reaction that was carried out below 120° C. This was done at the boiling point of toluene

(110°C.) The reaction vessel was fitted with an air condenser to avoid loss by evaporation.

TABLE IV

THERMAL DECOMPOSITION CONCENTRATIONS OF 1,4-BENZENEDISULFONYL AZIDE (RATIOS OF REACTANTS IN MOLE PER CENT)

Azide	Toluene	Azide	Xylene	Azide	Biphenyl
3.4	96.6	4.1	95.9	3.8	96.2
18.1	81.9	17.6	82.4	20.0	80.0
30.7	69.3	46.1	53.9	40.0	60.0
Azide	**Naphthalene**	**Azide**	**1,4-Dichloro-benzene**	**Azide**	**1,2,4,5-Tetra-chlorobenzene**
4.4	95.6	5.4	94.6	6.9	93.1
20.0	80.0	20.0	80.0	x	x
30.0	70.0	30.0	70.0	x	x
40.0	60.0	40.0	60.0	x	x

Isolation of Sulfonamides

Isolations of products were carried out in the following manner. Ten per cent sodium hydroxide was added to the reaction flask to dissolve and render extractable the desired reaction products. Extraction was continued with sodium hydroxide until the extract remained clear. The sodium hydroxide extracts were combined and heated to boiling. Decolorizing charcol (approximately 2 grams) was added and the solution was stirred for five minutes. The solution was filtered while hot, cooled and acidified with hydrochloric acid to precipitate the substituted sulfonamides. These were filtered off and dried.

The decompositions were first carried out for low azide concentrations and if a product was isolated by the above method, the concentration of

azide was increased as shown in Table IV. In all cases except that of 1,2,4,5-tetrachlorobenzene enough product was obtained to warrant further investigation. As the azide concentration was increased, the amount of expected product decreased, the reaction mixtures turned darker, and the products which were isolated also were darker. Product yields from decomposing 1,4-benzenedisulfonyl azide ranged from 22.6 to 90.0 per cent with the various reactants.

If a polymer were formed from the reaction of biphenyl and the 1,4-benzenedisulfonyl azide, it would have a repeating N-biphenylylbenzenedisulfonamide unit. Such a polymer was prepared by combining equimolar quantities of 1,4-benzenedisulfonyl chloride and benzidine, using separately sodium hydroxide, pyridine, and N,N-dimethylaniline as the hydrogen chloride acceptors. The reactants were heated at 100°C. for four hours and then acidified with hydrochloric acid. A product was formed that was plastic and pliable at 80°C. and above, but solidified on cooling to room temperature. This polymer is insoluble in all the common organic solvents that were tested. The polymer could be purified somewhat by dissolving in hot sodium hydroxide and precipitating again with hydrochloric acid.

For comparative purposes, absorption curves for appropriate compounds were made using a model 12-C Perkin-Elmer Infrared-Spectrometer. The compounds were ground to a fine powder and mineral oil was added until a mull was obtained. This mull was applied to the center of a sodium chloride crystal 2mm. thick and then was covered with another sodium chloride crystal. One crystal was rotated until it appeared that the compound was evenly distributed over the surface of the crystal. The spectrum of the compound was scanned between 9.5 and 14.5 microns, using an instrument gain of 14.5.

Figure 1 shows the spectra of mineral oil alone and the mulls of the polymers which were made from 1,4-benzenedisulfonyl chloride and benzidine using separately N,N-dimethylaniline and pyridine as the hydrogen chloride acceptors. Figure 2 shows the spectra of the products which were isolated after thermal decomposition of 1,4-benzenedisulfonyl azide in biphenyl with azide concentrations of 5.0, 20, 30 and 40 mole per cent. Figure 3 is a comparison of the spectrum of the polymer, made by metathesis, and the spectrum of the product made from the azide.

Preparation of Comparison Standards For The Reaction of 1,4-Benzenedisulfonyl Azide With Biphenyl And With Toluene

Five-hundredths mole of 1,4-benzenedisulfonyl chloride and 0.1 mole of 2-aminobiphenyl were combined in excess sodium hydroxide solution which served as a hydrogen chloride acceptor in the preparation of the N,N'-bis(2-biphenylyl)1,4-benzenedisulfonamide. This reaction was also carried out using 1,4-beznenedisulfonyl chloride and 4-aminobiphenyl. The suspensions were heated for four hours on a steam bath, treated with charcoal, filtered, and cooled, and the substituted sulfonamides were precipitated by adding concentrated hydrochloric acid. The precipitates were filtered off and washed several times with water to free them of excess acid.

Standards also were prepared for the reaction of 1,4-benzenedisulfonyl azide with toluene. These were prepared in a manner similar to the one given above and consisted of coupling 1,4-benzenedisulfonyl chloride, individually, with ortho, meta and para toluidines.

In Figure 4 is shown the spectrum of the isolated reaction product of 1,4-benzenedisulfonyl azide and biphenyl and the spectrum of a one-one

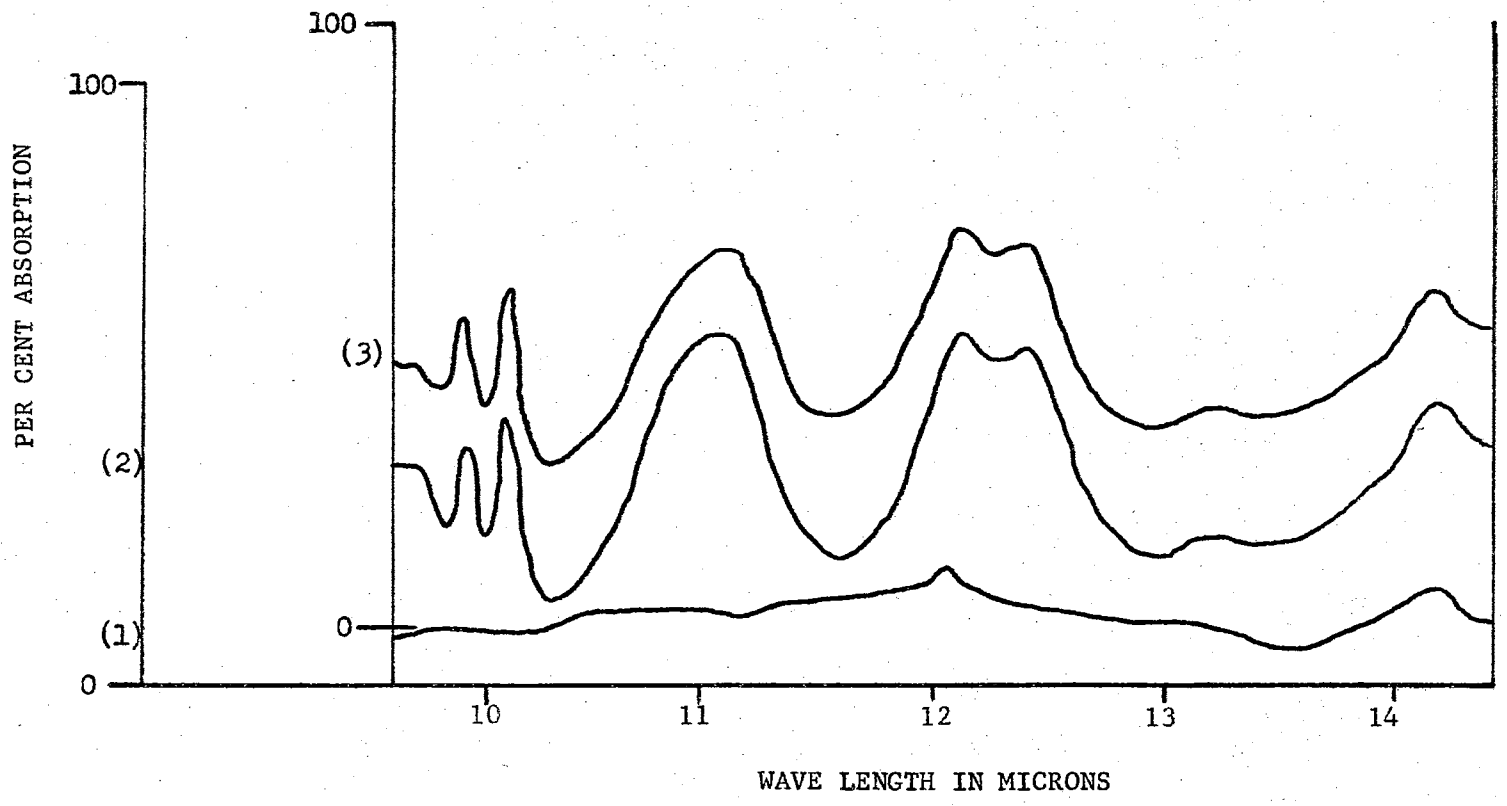


FIGURE 1: Absorption Curves of Mineral Oil (1), Polymer Made From 1,4-Benzenedisulfonyl Chloride and Benzidine With Pyridine (2) and N,N-Dimethyl Aniline (3) as Hydrogen Chloride Acceptors.

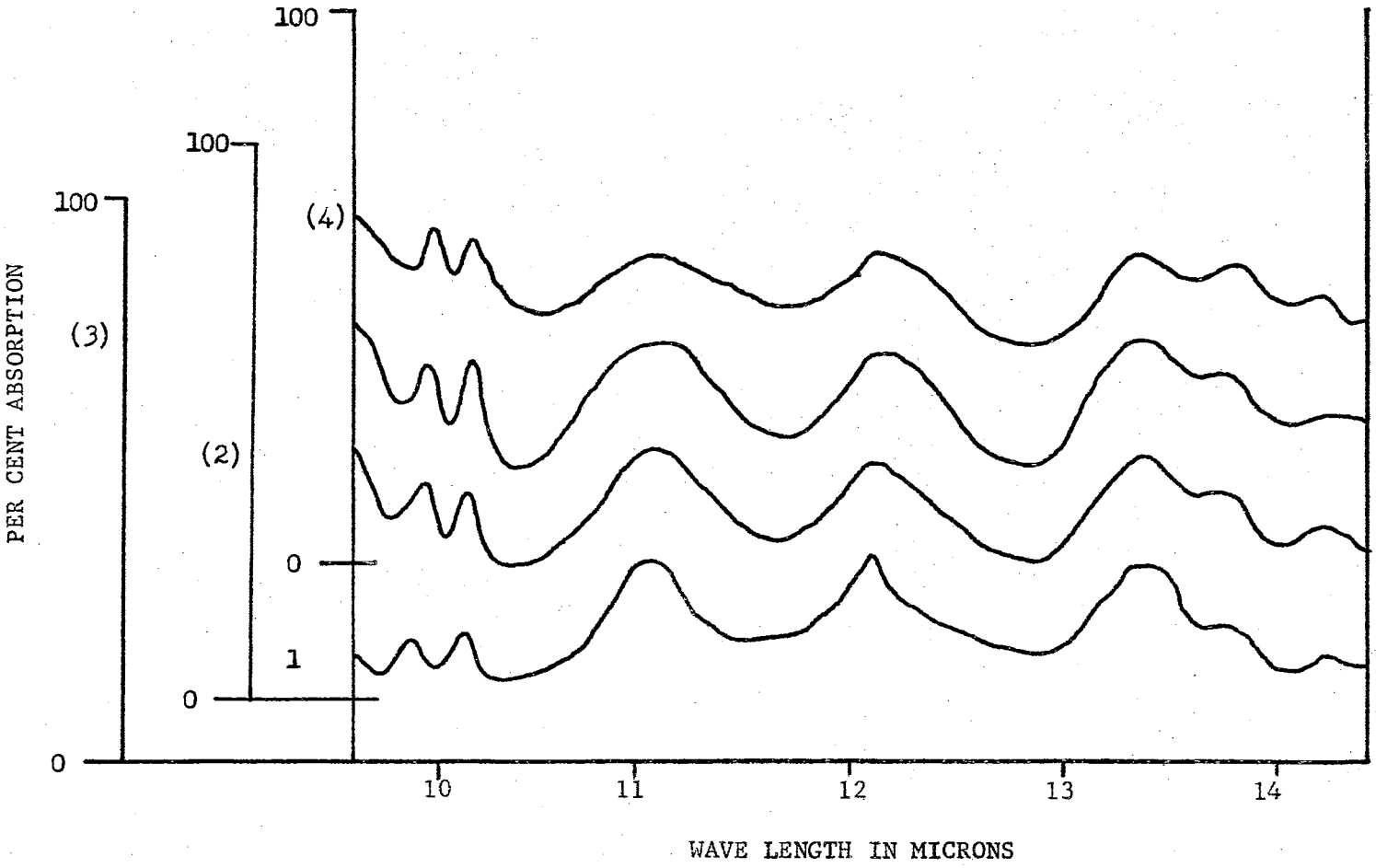


FIGURE 2: Absorption Curves of The Products From Decomposition of 1,4-Benzenedisulfonyl Azide in Biphenyl at Azide Concentration of 3.8 (1), 20 (2), 30 (3) and 40 (4) Mole Per Cent.

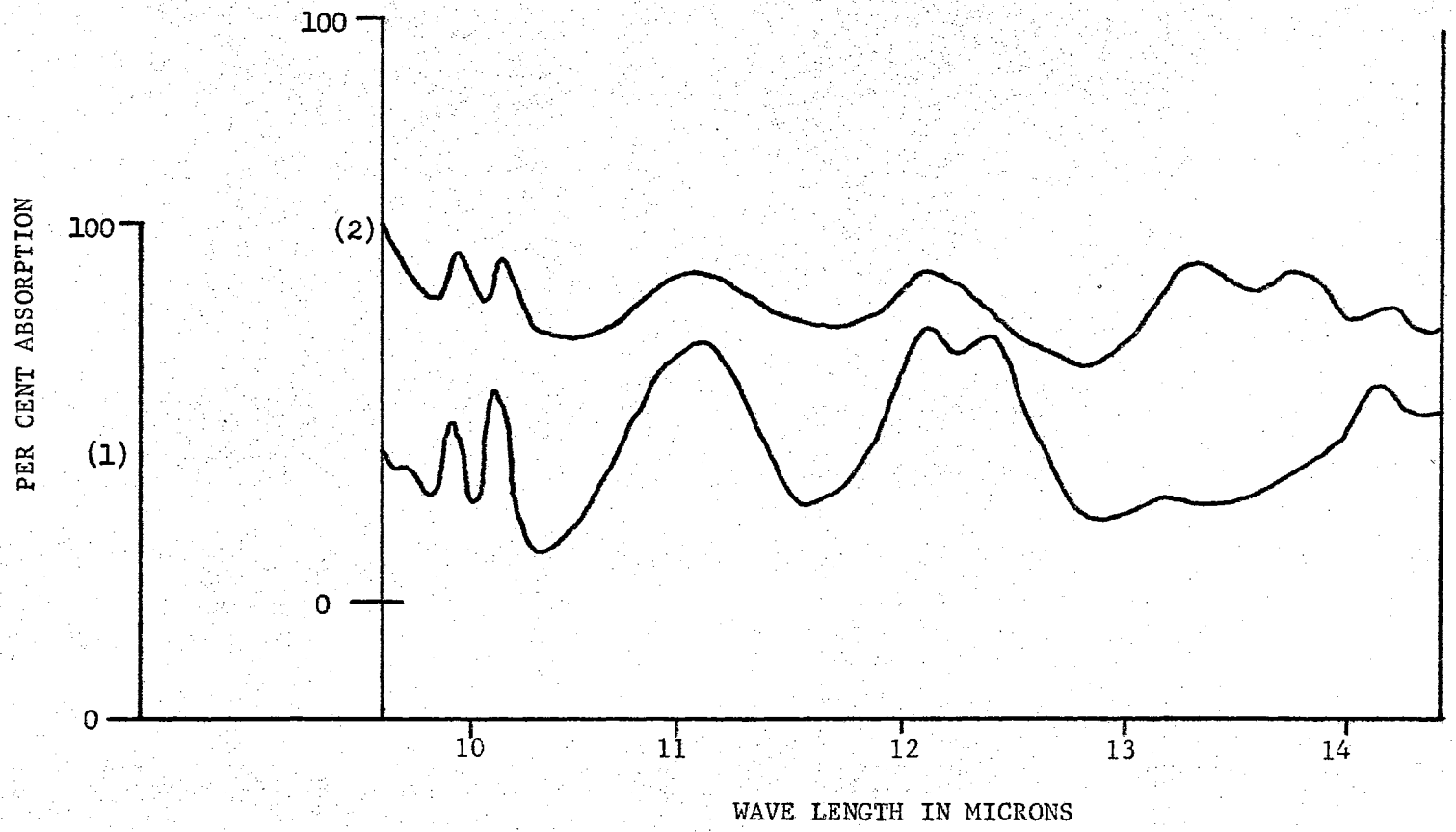


FIGURE 3: Absorption Curves for the Polymer Prepared From 1,4-Benzenedisulfonyl Chloride and Benzidine (1) and The Product From Decomposition of 40 Mole Per Cent 1,4-Benzenedisulfonyl Azide in Biphenyl (2).

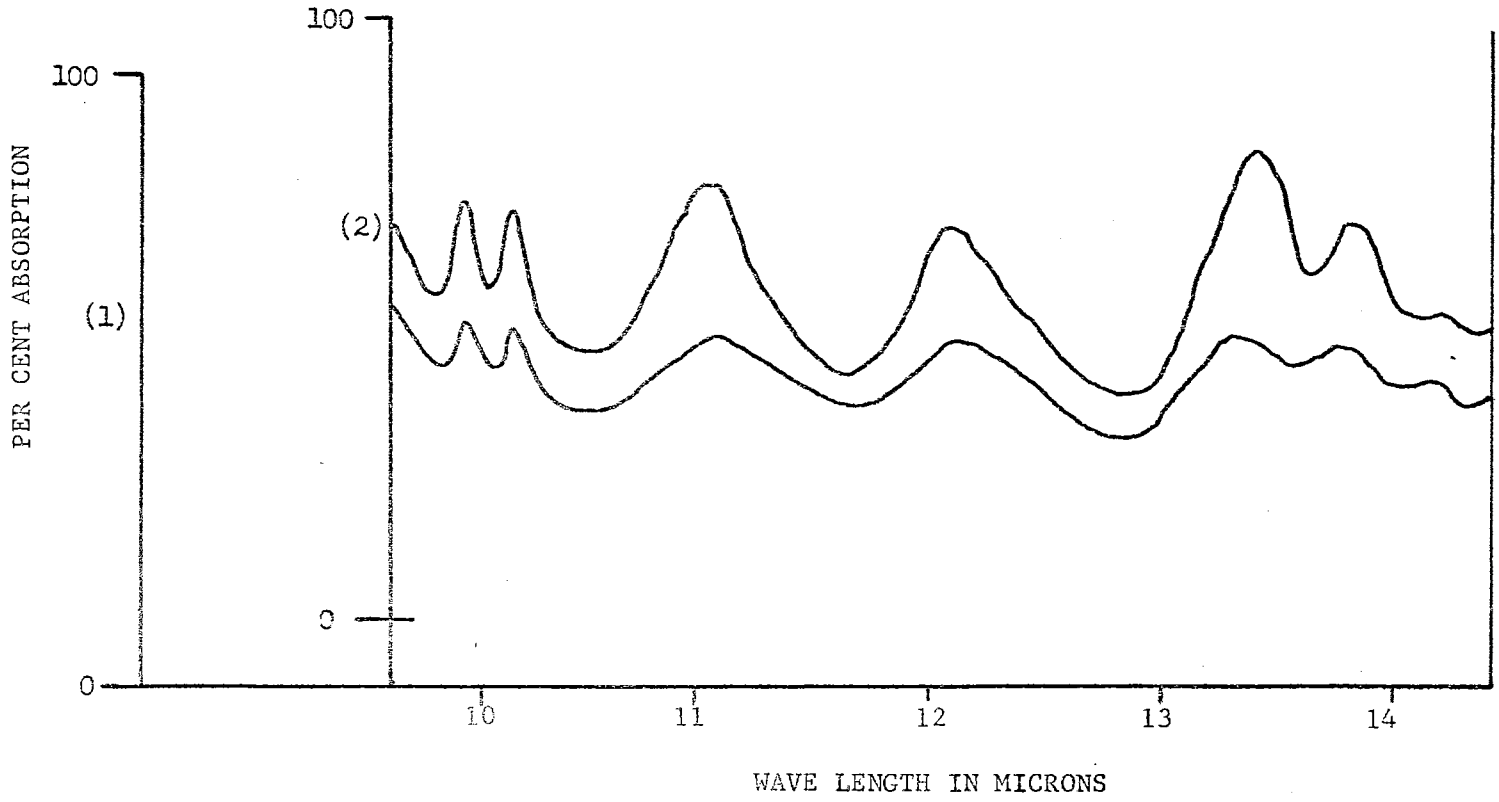


FIGURE 4: Absorption Curves of a One to One Mixture of N,N'-bis (4-Biphenylyl) 1,4-Benzenedisulfonamide and N,N'-bis (2-Biphenylyl) 1,4-Benzenedisulfonamide (1) and The Product From Decomposition of 40 mole Per Cent 1,4-Benzenedisulfonyl Azide in Biphenyl (2).

mixture of N,N'-bis(2-biphenylyl)-1,4-benzenedisulfonamide and N,N'-bis(4-biphenylyl)-1,4-benzenedisulfonamide.

The spectra were determined for the isolated reaction products of 1,4-benzenedisulfonyl azide and toluene. The spectra were also determined for the corresponding 1,4-benzenedisulfontoluidides and they were inspected for characteristic absorption peaks. All of the peaks appeared in the spectrum of the reaction product from the decomposition of azide in toluene, but owing to the number of possible isomers, the correct ratio to produce a matching spectrum was not attained in a mixture. An attempt was made to determine the amounts of the ortho, meta and para isomers which were present in the reaction product from azide decomposition. An effective solvent that did not absorb in the region of 9.5 to 14.5 microns, was needed. However, such a solvent was not found.

Methyl Cellosolve Extraction

The lower-molecular-weight disulfonamides are soluble in hot methyl Cellosolve while the polymer is insoluble. Therefore, using a Soxhlet extractor and methyl Cellosolve as a solvent, the polymer prepared from 1,4-benzenedisulfonyl chloride and benzidine was extracted for 24 hours. The products from the decomposition of different mole ratios of the 1,4-benzenedisulfonyl azide decomposed in biphenyl were also extracted 24 hours with methyl Cellosolve. In this manner, it was hoped to get a separation of the products from the decomposition of the azide in biphenyl. After extraction had been continued for 24 hours, only the product from the solution containing 20 per cent mole ratio of azide was there appreciable residue and this was less than 1 per cent of the starting material. A

spectrum was determined on this insoluble material, but it did not match the spectrum of the standard polymer.

Attempt at Further Substitution

In order for a polymer to form, it would be necessary for the decomposing azide to make a second attack on the sulfonamide already formed. This apparently was not taking place. In order to find out if a second attack was possible, a sulfonamide that had a melting point at or below the decomposition temperature of the azide was needed. Such a compound was N-(p-tolyl)benzenesulfonamide with a literature melting point of 120°C. This compound was prepared from benzenesulfonyl chloride and p-toluidine in equivalent amounts. Ten per cent sodium hydroxide solution was used as the hydrogen chloride acceptor. The reactants were heated at 90° for four hours, treated with charcoal, filtered and cooled. The sulfonamide was precipitated by adding concentrated hydrochloric acid. It was recrystallized from ethyl ether and these melted at 119°C. This sulfonamide then was heated until it just melted and enough benzenesulfonyl azide was added to make a 5 mole per cent solution; the decomposition was allowed to proceed for 120 hours.

If a second attack occurred, it was assumed that it would be on the benzene ring in the tolyl radical and thus it could produce only two isomers, although there is a possibility of attack at four equivalent positions. These compounds would be N,N'-(4-methyl-m-phenylene)bis-benzenesulfonamide and N,N'-(4-methyl-o-phenylene)bis-benzenesulfonamide. Authentic specimens were prepared by combining the appropriate toluenediamine with benzenesulfonyl chloride in a 10 per cent sodium hydroxide solution. The solution was heated

at 90°C. for four hours, treated with charcoal, filtered and acidified with concentrated hydrochloric acid to precipitate the product. Their melting points were 190°C. and 177°C., respectively, compared with the literature values of 191°C. and 178°C.- 179°C.

The azide-sulfonamide mixture, after reacting 120 hours, was extracted with sodium hydroxide, heated, treated with charcoal and acidified with hydrochloric acid. All of the N-tolyl derivatives, including the substrate, are alkali-soluble and were separated in this manner from the crude reaction mixture. The precipitate was dried and extracted with ethyl ether, in which the expected disulfonamides are insoluble. The whole mass of dried product went into solution. This was evidence that the desired products did not form. The ether was evaporated and six different fractions were obtained by crystallization. Absorption spectra were obtained on these and compared to the spectra of the standards mentioned above. The six spectra were identical and matched the spectrum of the substrate. A product was isolated from the acid filtrate by evaporation of the filtrate and extraction with acetone. This compound has not been positively identified but it is thought to be the main reaction product; the spectrum is similar to that of sodium benzenesulfonate. This product was soluble in both aqueous acid and aqueous base and thus can hardly be the desired product.

The above procedure was repeated using a 10 per cent mole ratio of azide to sulfonamide. The results substantiated the results of the first trial.

Thermal Decomposition of 1,4-Benzenedisulfonyl Azide Alone

A number of samples of 1,4-benzenedisulfonyl azide were decomposed at 120°C. The azide turned to a brown liquid after about 6 hours and was completely black after 10 hours. After heating for 168 hours, a sample was treated with excess phosphorus pentachloride and the black mass was converted to the 1,4-benzenedisulfonyl chloride in a 79 per cent yield. That the product was the disulfonyl chloride was confirmed by a mixed melting point.

When a sample of azide is decomposed at 120°C. with a calcium chloride drying tube in place, the decomposition products form as a black powder; otherwise they are so deliquescent that they take up water when the vessel is open to the air even at a temperature of 120°C. When the products of decomposition were dissolved in water, in which they are completely soluble, the solution, even in low concentration of products, is very acidic. The amount of acid present was determined by titrating with standard base to a pH of 7, using a model H-2 Beckmann pH meter. When 10 per cent sodium hydroxide was added to the decomposed azide, the odor of ammonia was noted. The amount of ammonia was determined by adding excess sodium hydroxide and distilling. The distillate was collected in standard acid and finally back-titrated with standard base. Calculated values from these determinations, based upon 1,4-benzenedisulfonic acid and its monoammonium salt, were 0.0026 mole of acid and 0.0025 mole of monoammonium salt. This gave a ratio of free acid groups to ammonium salt of three to one. The experimental data from which these computations were made varied less than 3 per cent from the average value. The average yield of the two together was 73.9 per cent based on 0.0069 mole of 1,4-benzenedisulfonyl azide.

A sample of decomposition products in water solution, when treated wit a known amount of charcoal (1 gram per gram of azide) and filtered, gives a clear light yellow filtrate. By drying and weighing the charcoal, it was shown for different samples that between 1.5 and 3.0 per cent of the material is adsorbed by the charcoal. The filtrate on standing turns to a light red color, owing to the formation of a dye, that can be removed by charcoal. After five treatments with charcoal over a period of two weeks the solution no longer became colored. The solution was evaporated and the absorption spectrum was determined for the dry material by using a mineral oil mull. A standard was obtained by treating the potassium 1,4-benzenedisulfonate with concentrated hydrochloric acid and evaporating. The residue then was taken up in water and a half mole equivalent of ammoni hydroxide was added to half neutralize the acid and obtain the half ammoniu salt of 1,4-benzenedisulfonic acid. These spectra are compared in Figure 5. The spectrum of the standard matches the spectrum of the unknown from the decomposed azide that was isolated by the method described above. However, since the standard was prepared as it was, the amount of ammonium salt present is doubtful. It is thought that the spectra (Fig. 5) show only the benzenesulfonate groups and not the cations. The ammonium ion should absorb, but presumably it is blacked out by the mineral oil.

Two samples of 1,4-benzenedisulfonyl azide decomposed at 120°C. with a 12-cm. calcium chloride drying tube in place were weighed periodically until constant weight was obtained. This was after 120 hours. The weight-loss was 24.27 and 24.28 per cent. If five-sixths of the theoretical nitrogen present was given off the weight loss would be 24.30 per cent; this would be the correct value for a one to one ratio of sulfonic acid

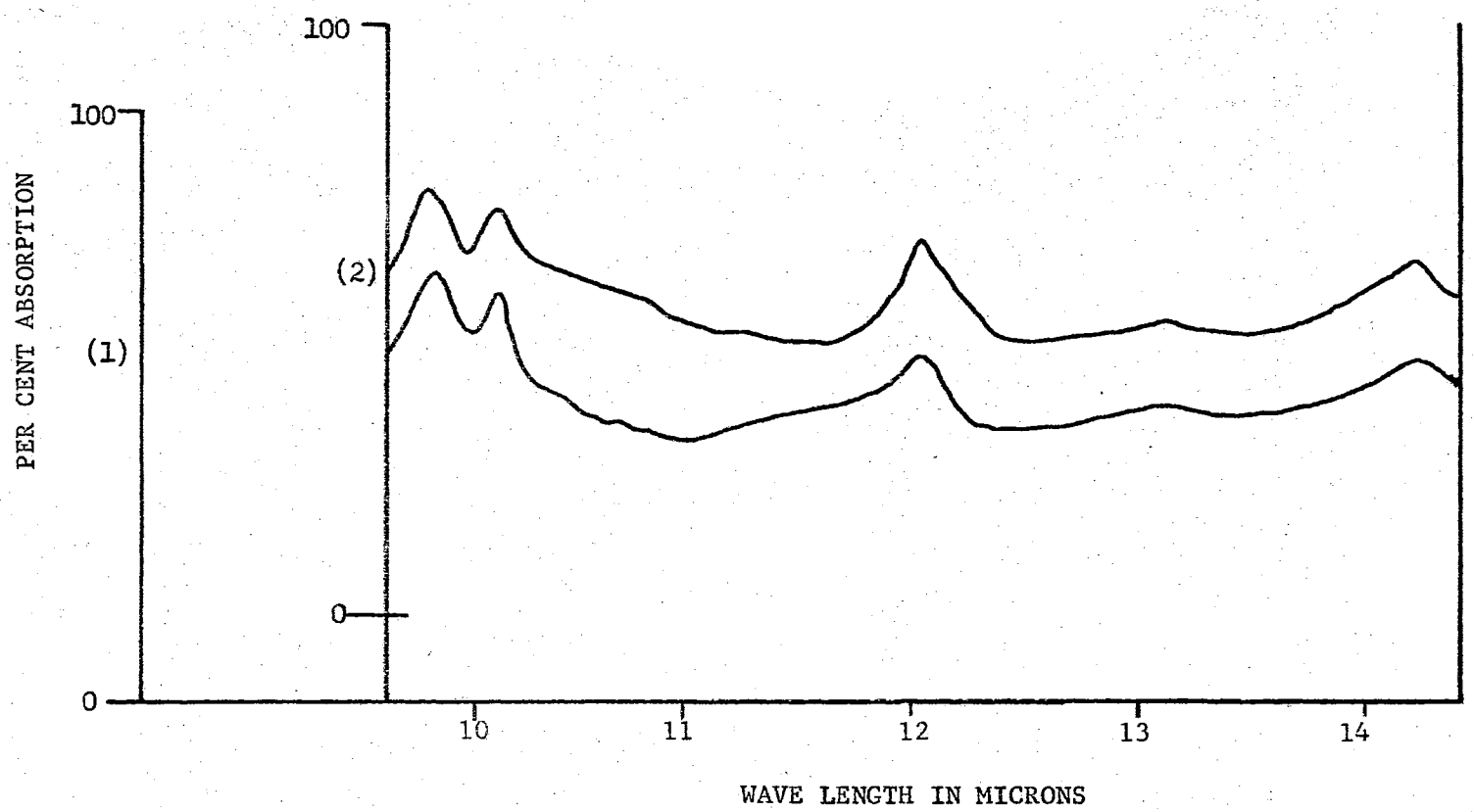


FIGURE 5: Absorption Curves of Potassium 1,4-Benzenedisulfonate (1), and the Product From 1,4-Benzenedisulfonyl Azide Decomposed Alone (2).

to ammonium sulfonate. Apparently some of the nitrogen remains in the product which was adsorbed on the charcoal.

Gas Collections From 1,4-Benzenedisulfonyl Azide

The apparatus used for the collection of nitrogen gas from the decomposing azide was a closed system containing a reaction vessel that could be heated in a wax bath at 120°C. Air was flushed from the system by the use of carbon dioxide and the carbon dioxide was collected in a bulb containing 30 per cent sodium hydroxide, fitted with a three-way stopcock that could be opened to the outside air or to a gas burette. A leveling bulb was used to force the collected air out of the apparatus while the rest of the system was closed to the air. When the collected air had been released the stopcock was again opened to the system which then was full of carbon dioxide. In each case, heating of the azide samples, both with and without a substrate, was started at 120°C. and continued until no gas was evolved for a 24-hour period. The system, when cool, was again swept with carbon dioxide to force the nitrogen into the collection bulb and leave the system full of carbon dioxide. The stopcock was then turned so that it was closed both to the air and to the system. The bulb was shaken to absorb the excess carbon dioxide and left for a period of 12 hours to be certain that the absorption of carbon dioxide was complete. The gas was then collected over water in a gas burette and the volume was converted to milliliters at standard temperature and pressure.

Results of Gas Collections From 1,4-Benzenedisulfonyl Azide

In each case, 2.0000 grams (0.0069 mole) were used for the gas collection experiments. The results are summarized in Table V below.

TABLE V

GAS COLLECTED FROM THERMAL DECOMPOSITIONS OF
1,4-BENZENEDISULFONYL AZIDE IN
BIPHENYL SUBSTRATE AND ALONE

Mole Per Cent 1,4-Benzenedisulfonyl Azide	Gas Collected Ml. at S.T.P.	Sulfonamide[1] Isolated Product (Per Cent)
5.0	305, 315, 318	67.1
9.7	309, 312	63.9
17.5	310, 302, 318	63.9
29.8	345, 343	28.8
34.7	347, 341	28.8
100.0	386, 388	----

[1] To calculate the per cent yield, the sulfonamide isolated was considered to be a N,N'-bis(x-biphenylyl)-1,4-benzenedisulfonamide.

If, on heating, 4 of the 6 nitrogen in each molecule of azide are released, the amount of gas evolved will be 310 ml.; if 5 of the 6 nitrogen atoms are released, the amount will be 388 ml.; and if all the nitrogen is released, there will be 466 ml. of nitrogen gas evolved. The substrate in all cases was biphenyl. Usually two experiments were made at each concentration. However, if the results did not agree reasonable well a third was made. The percentage yield of product is the amount of product (based on .0069 mole) isolated from only the first gas collection, e.g., from the sample that evolved 305 ml. of nitrogen, there was isolated .0039 mole of product which is 67 per cent yield if the identity of the product is assumed as N,N'-bis(x-biphenylyl)-1,4-benzenedisulfonamide.

After all the nitrogen released by heating 1,4-benzenedisulfonyl azide had been collected, Kjeldahl analyses were run to determine the amount of nitrogen remaining. This was found to be 4.44 and 4.56 per cent in duplicate experiments.

Thermal Decomposition of 1,3-Benzenedisulfonyl Azide

Decomposition of 1,3-benzenedisulfonyl azide was carried out in the same manner as the decomposition of 1,4-benzenedisulfonyl azide that was previously described. The substrates were the same. The summary of these decompositions are given below in Table VI. They are reported in mole per cent.

TABLE VI

THERMAL DECOMPOSITION CONCENTRATIONS OF 1,3-BENZENEDISULFONYL AZIDE (RATIOS OF REACTANTS IN MOLE PER CENT)

Azide	Toluene	Azide	Xylene	Azide	Biphenyl
3.4	96.6	4.1	95.9	3.8	96.2
30.0	70.0	30.0	70.0	30.0	70.0
Azide	**Naphthalene**	**Azide**	**1,4-Dichlorobenzene**	**Azide**	**1,2,4,5-Tetrachlorobenzene**
4.4	95.6	5.4	94.6	5.0	95.0
30.0	70.0	30.0	70.0	x x	xx x

Products were isolated in the same way as the reaction products from the decomposition of 1,4-benzenedisulfonyl azide. Product yields with the various substrates ranged from 21.0 to 79.3 per cent. Standards for infrared comparison with products from the reaction were made by using 1,3-benzenedisulfonyl chloride and 2- and 4-amino biphenyls. The standards were isolated in the same manner as the products from the 1,4-benzenedisulfonyl azide decompositions. Infrared absorption spectra are shown in Figure 6 for the products which were isolated after the thermal decomposition of 1,3-benzenedisulfonyl azide in 5.0, 9.7, 17.5, and 29.8 mole per cent azide in biphenyl. Infrared absorption spectra shown in

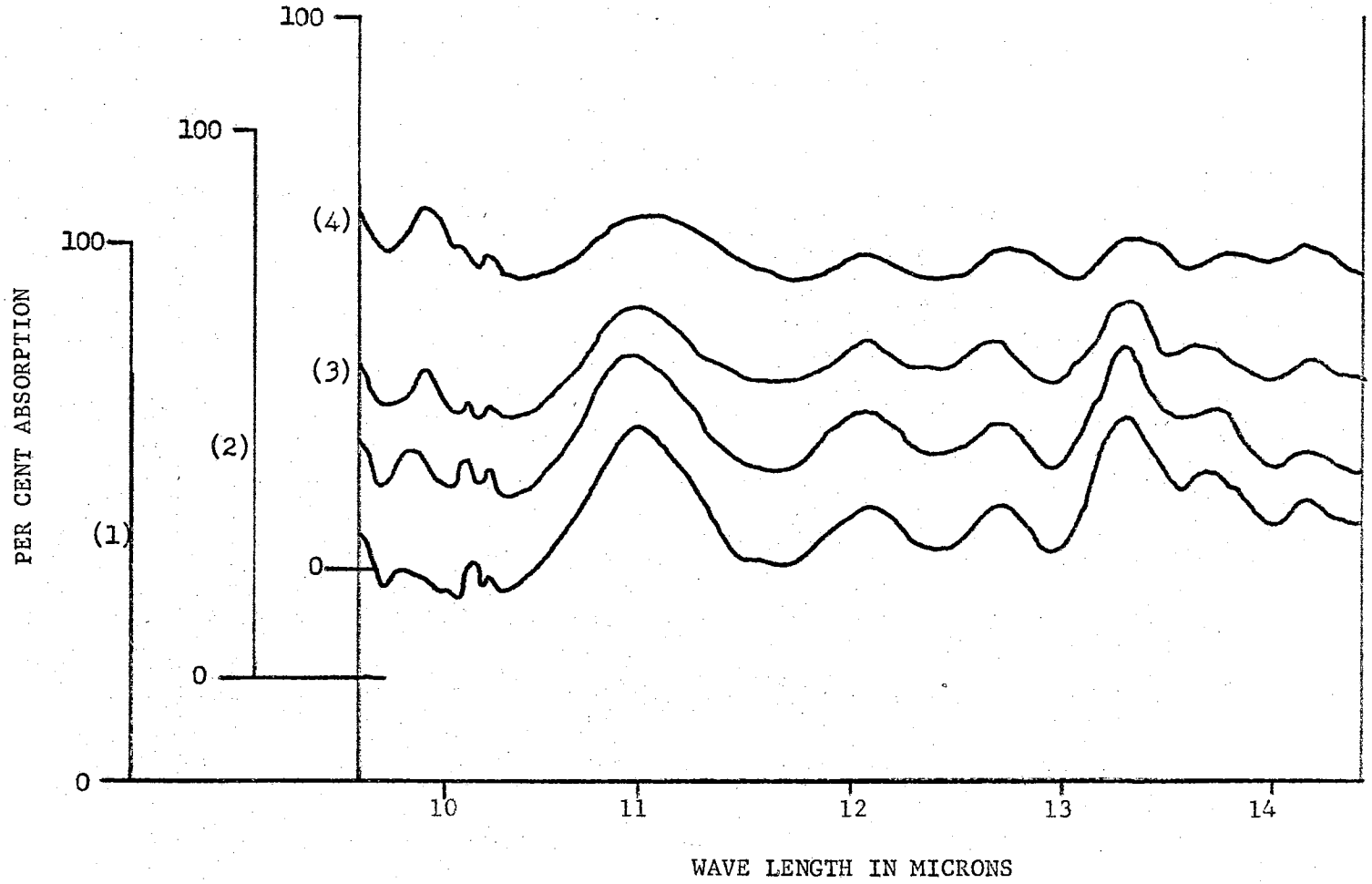


FIGURE 6: Absorption Curves of the Product From the Decomposition of 1,3-Benzenedisulfonyl Azide in Biphenyl at Azide Concentrations of 5.0 (1), 9.7 (2), 17.5 (3) and 29.8 (4) Mole Per Cent.

Figure 7 are for the product of the thermal decomposition of 1,3-benzenedisulfonyl azide in biphenyl (20 mole per cent azide) and for a one to one mixture of the two standards prepared from the reaction of the 1,3-disulfonyl chloride and 2- and 4-amino biphenyl, separately.

The 1,3-benzenedisulfonyl azide also was decomposed alone at 120°C. A black liquid was obtained when the system was open to the air, but when it was closed with a calcium chloride drying tube a black, very deliqueiscent solid was obtained. This black material was converted to 1,3-benzenedisulfonyl chloride in an 86 per cent yield by treating with phosphorus pentachloride. When heated at 120°C., with a calcium chloride drying tube in place, until constant weight was reached, the diazide lost 26.05 and 26.28 per cent in weight in two experiments. If 5 of the 6 atoms of nitrogen present per molecule had been released, the weight loss would be 24.30 per cent as for the 1,4-benzenedisulfonyl azide.

Solutions of samples of decomposition products from 1,3-benzenedisulfonyl azide were titrated with standard sodium hydroxide, the same as for 1,4-benzenedisulfonyl azide, to determine the amount of acid present. Other samples were treated with excess sodium hydroxide in the same manner as products from 1,4-benzenedisulfonyl azide, in order to calculate the amount of ammonium salt present. The results, calculated as 1,3-benzenedisulfonic acid, showed 0.0037 mole of acid and 0.0010 mole of monoammonium salt of 1,3-benzenedisulfonic acid. This gave a ratio of free acid groups to ammonium salt of 3.7 to 1. The total yield was 68.1 per cent based on 0.0069 mole of 1,3-benzenedisulfonyl azide.

The products from the decomposition of 1,3-benzenedisulfonyl azide were completely water-soluble, like the products from the decomposed 1,4-benzenedisulfonyl azide. They were treated with charcoal and the solution

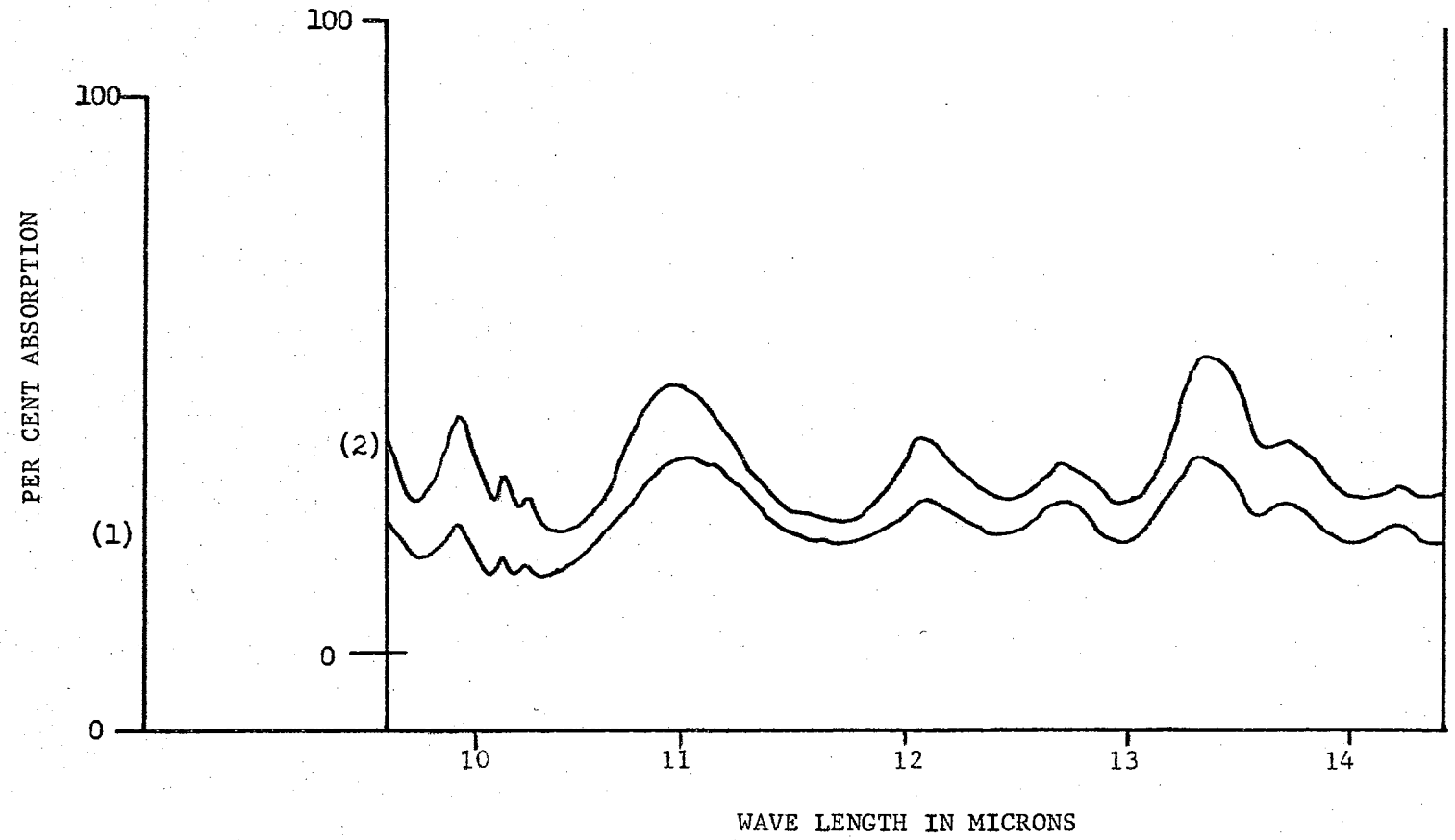


FIGURE 7: Absorption Curves of the Product from Decomposition of 17.5 Mole Per Cent 1,3-Benzenedisulfonyl Azide in Biphenyl (1) and a One to One Mixture of N,N'-bis(2-Biphenylyl)-1,3-Benzenedisulfonamide and N,N'-bis(4-Biphenylyl)-1,3-Benzenedisulfonamide (2).

was colorless until it had been standing for a few hours, after which a color appeared, presumably due to the formation of an unknown dye. This dye, like the one formed by the decomposition of 1,4-benzenedisulfonyl azide, could be removed by further treatment with charcoal. After treating with charcoal 5 times (using 2 grams of charcoal each time the solution turned color), the color did not develop to any appreciable extent. When the color no longer developed, the solution was neutralized with sodium hydroxide and then evaporated to dryness. The infrared absorption spectrum of the product was then compared to that of standard sodium 1,3-benzenedisulfonate (made from neutralizing commercially available 1,3-benzenedisulfonic acid). These spectra are shown in Figure 8.

The amount of material adsorbed by 1 gram of charcoal per gram of azide also was determined and found to be 14 to 14.5 per cent. The material adsorbed was either colloidal or water-soluble as it could not be separated by filtration even when very retentive filters were used.

Results of Gas Collections From 1,3-Benzenedisulfonyl Azide

The same apparatus as was used with the 1,4-benzenedisulfonyl azide was used for collecting gas from the decomposition of 1,3-benzenedisulfonyl azide. Biphenyl was the substrate and the amount of 1,3-benzenedisulfonyl azide for each determination was 2.0000 grams. The theoretical amount of gas is the same as for the same amount of 1,4-benzenedisulfonyl azide, i.e., 310 ml. for nitrogen atoms released per azide molecule, 388 for 5 nitrogen atoms and 466 for 6 nitrogen atoms. The results of the gas collections are shown in Table VII.

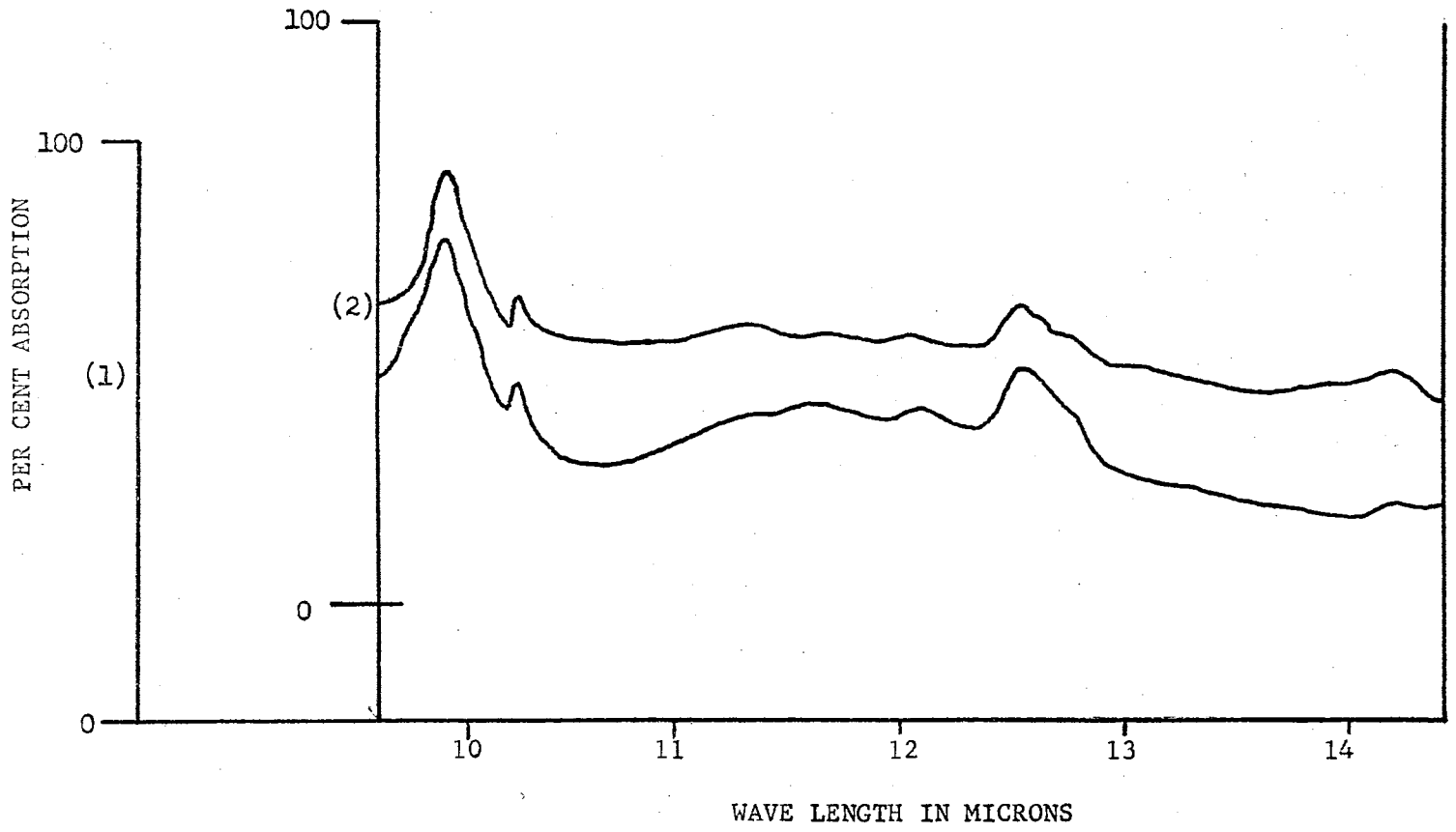


FIGURE 8: Absorption Curves of the Product From 1,3-Benzenedisulfonyl Azide Decomposed Alone (1) and Sodium 1,3-Benzenedisulfonate (2).

TABLE VII

GAS COLLECTED FROM THERMAL DECOMPOSITIONS OF
1,3-BENZENEDISULFONYL AZIDE IN
BIPHENYL SUBSTRATE AND ALONE

Mole Per Cent 1,3-Benzenedisulfonyl Azide	Gas Collected Ml. at S.T.P.	Sulfonamide[1] Isolated Product (Per Cent)
5.0	313, 312	63.9
9.7	312, 306	60.7
17.5	313, 307	60.7
29.8	321, 317	25.6
34.7	339, 346	25.6
100.0	414, 420	----

[1] To calculate the per cent yield, the sulfonamide isolated was considered to be a N,N'-bis(x-biphenylyl)-1,3-benzenedisulfonamide.

The amount of nitrogen left after decomposition was also determined for the 1,3-benzenedisulfonyl azide, by Kjeldahl analysis of the residue and was found to be 3.00 and 3.25 per cent from duplicate experiments.

Thermal Decompositions of 4,4'-Biphenyldisulfonyl Azide and 1,5-Naphthalene Disulfonyl Azide

Decompositions were carried out as described previously except that the temperature was 135°C. The substrates and mole ratios are listed in Table VIII. Products were isolated in the same manner as previously described. Product yields ranged from 22.0 to 68.4 per cent. Standards for infrared analysis were prepared and isolated only from the reaction of 4,4'-biphenyldisulfonyl chloride and 2- and 4-aminobiphenyls, respectively. The infrared spectra of these compounds are compared in Figures 9 and 10.

The 4,4'-biphenyldisulfonyl azide was decomposed alone at 135°C. with a calcium chloride drying tube in place. A black solid material was

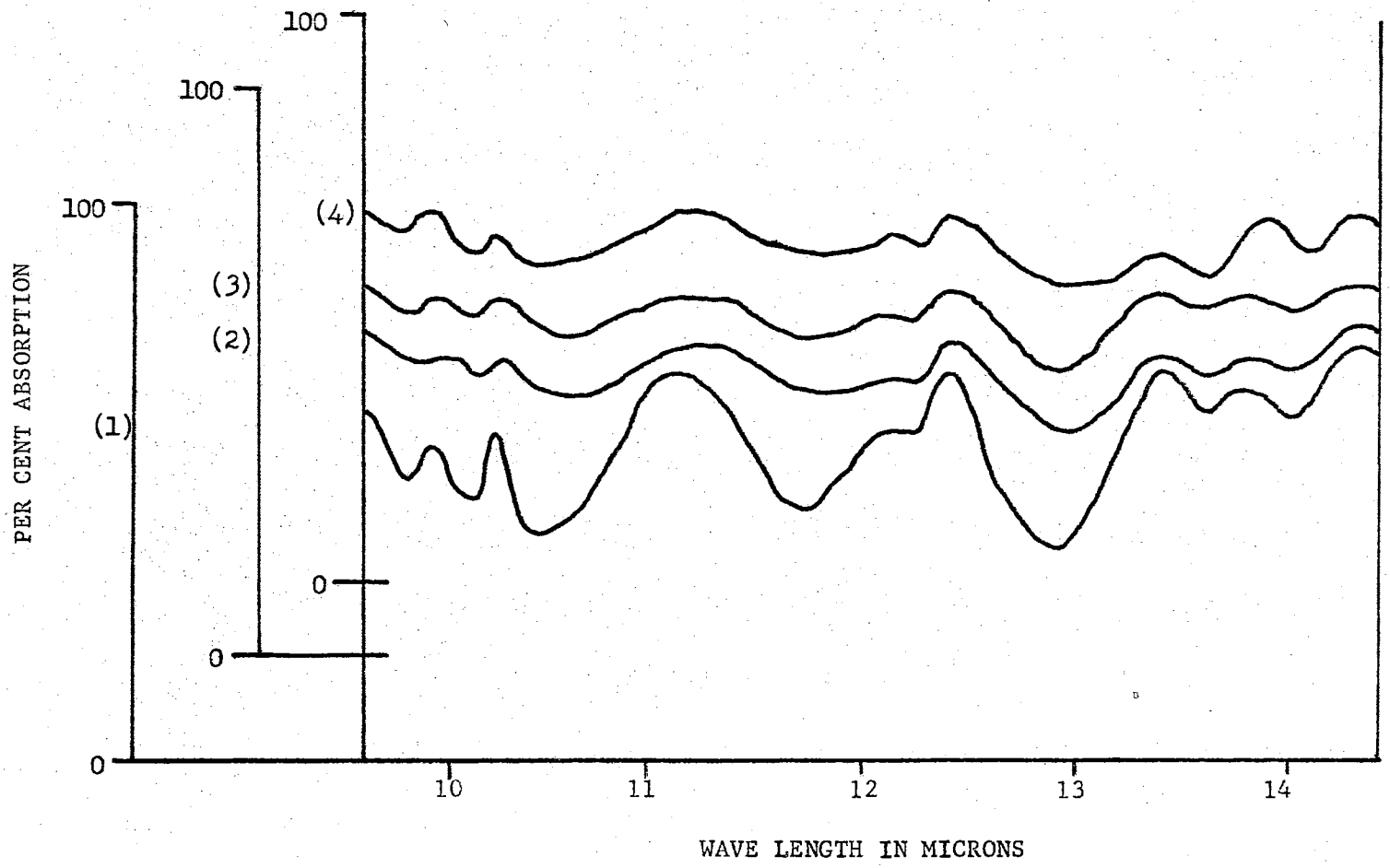


FIGURE 9: Absorption Curves of the Product from the Decomposition of 4,4'-Biphenyldisulfonyl Azide in Biphenyl at Azide Concentrations of 5.0 (1), 9.7 (2), 17.5 (3) and 29.8 (4) Mole Per Cent.

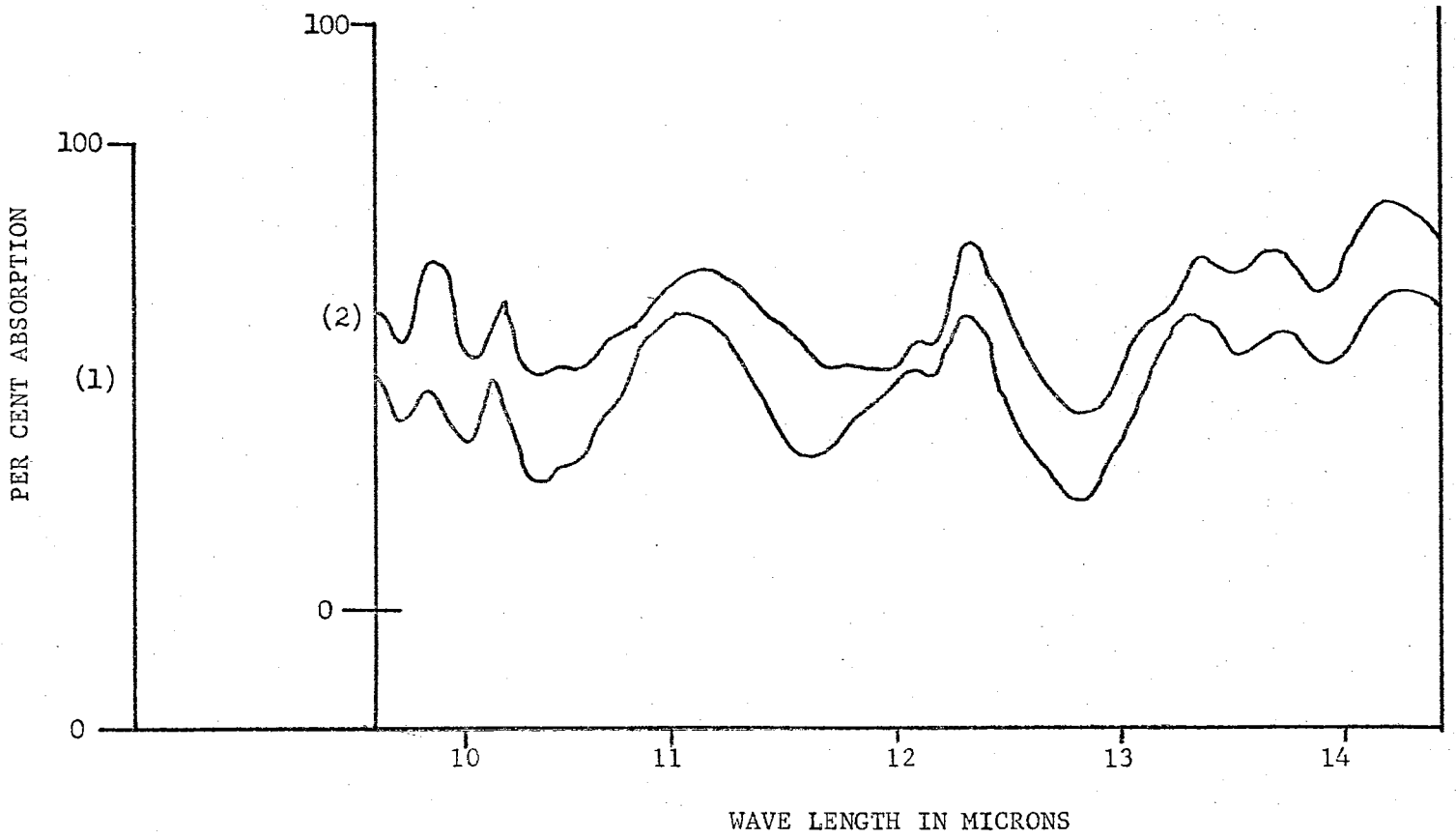


FIGURE 10: Absorption Curves of the Product from the Decomposition of 5.0 Mole Per Cent 4,4'-Biphenyldisulfonyl Azide in Biphenyl (1) and a One to One Mixture of N,N'bis(2-Biphenylyl)-4,4'-Biphenyldisulfonamide and N,N'-bis(4-Biphenylyl)-Biphenyldisulfonamide (2).

obtained. Loss in weight was 19.11 and 19.19 per cent. If five of the 6 nitrogen atoms were evolved the loss would be 19.22 per cent.

TABLE VIII

THERMAL DECOMPOSITION CONCENTRATIONS OF 4,4'-BIPHENYLDISULFONYL AIZDE
(RATIOS OF REACTANTS IN MOLE PER CENT)

Azide	Toluene	Azide	p-Xylene	Azide	Biphenyl
2.9	97.1	3.2	96.8	4.1	95.9
30.0	70.0	30.0	70.0	30.0	70.0

Azide	Naphthalene	Azide	p-Dichlorobenzene
3.4	96.6	3.6	96.4
30.0	70.0	30.0	70.0

THERMAL DECOMPOSITION CONCENTRATIONS 1,5-NAPHTHALENEDISULFONYL AZIDE
(RATIOS OF REACTANTS IN MOLE PER CENT)

Azide	Toluene	Azide	p-Xylene	Azide	Biphenyl
3.0	97.0	3.5	96.5	4.4	95.6
30.0	70.0	30.0	70.0	30.0	70.0

Azide	Naphthalene	Azide	p-Dichlorobenzene
3.8	96.2	3.9	96.1
30.0	70.0	30.0	70.0

Samples of 4,4'-biphenyldisulfonyl azide were titrated with standard base, as previously described for other azides, to determine the amount of acid present. The amount of ammonium salt present was also determined as previously described. These determinations indicated the presence of .0036 mole of 4,4'-biphenyldisulfonic acid and .0006 mole of monoammonium salt of 4,4'-biphenyldisulfonic acid. This gave a ratio of free acid groups to ammonium salt of six to one. The yield was 60.9 per cent based on .0069 mole of 4,4'-biphenyldisulfonyl azide.

The products from decomposing the 4,4'-biphenyldisulfonyl azide are not completely water-soluble and some of them can be filtered off.

However, the filtrate is still black. It was found that the total insoluble material adsorbed, using 1 gram of charcoal per gram of azide, was 17.7 to 18.4 per cent. Upon treating twice with charcoal, the solution was a light yellow and retained this color. The presence of a dye was not as pronounced as with the other azides previously described. Upon neutralization with sodium hydroxide and evaporation of the yellow filtrate, a salt was produced which was shown by means of infrared spectra to be sodium 4,4'-biphenyldisulfonate. The spectra are compared in Figure 11.

Results of Gas Collection From 4,4'-Biphenyldisulfonyl Azide

Gas collections were made as previously described. Biphenyl was the substrate and the amount of azide was 3.52769 (.0069 mole) which is equivalent to 2.0000 grams of either 1,3- or 1,4-benzenedisulfonyl azide. By using this amount, the theoretical volume of gas will be the same, i.e., 4 nitrogen atoms released will produce 310 ml. of gas, 5 atoms will produce 388 ml. and 6 will produce 466 ml. The results of the gas collections are shown in Table IX.

Decompositions of Other Aromatic Azides

Some experimental work was done with benzenesulfonyl azide and part of this has already been discussed. Difficulty was encountered in gas collection when this azide was decomposed alone. It vaporized to the cooler portion of the reaction vessel and thus decomposition was not completed.

Experimental work on 4-nitrobenzenesulfonyl azide was also minimal. The preparation has already been described. The compound has not been

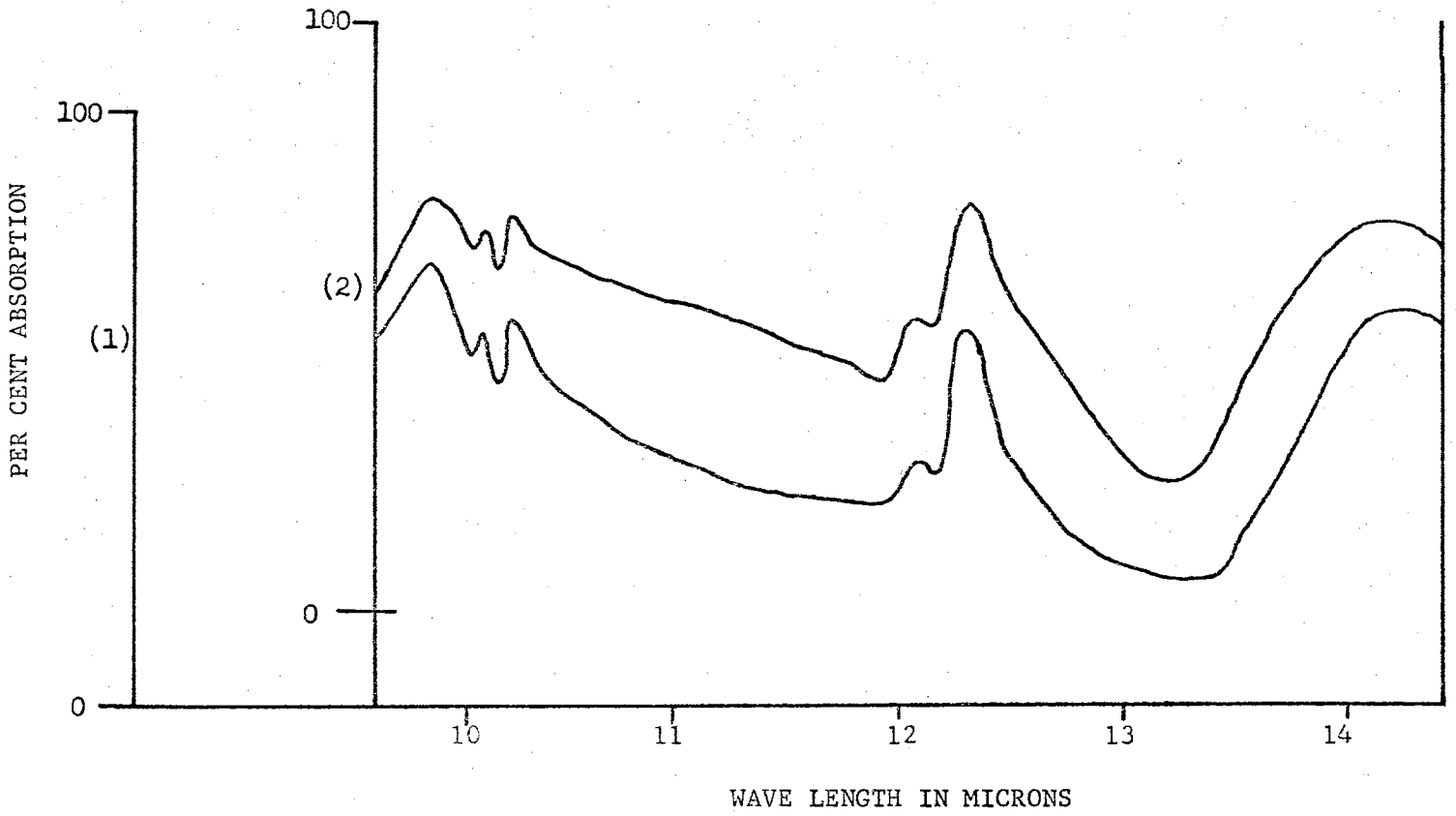


FIGURE 11: Absorption Curves of the Product from 4,4'-Biphenyldisulfonyl Azide Decomposed Alone (1) and Sodium 4,4'-Biphenyldisulfonate (2).

reported in the literature. It has a melting point of 100°C. and decomposes smoothly at 120°C. It was hoped that the compound could be used to study the effect of a para-nitro versus a para-sulfonyl azide group. Results were inconclusive owing to sublimation of the compound.

TABLE IX

GAS COLLECTED FROM THERMAL DECOMPOSITIONS OF 4,4'-BIPHENYLDISULFONYL AZIDE IN BIPHENYL SUBSTRATE AND ALONE

Mole Per Cent 4,4'-Biphenyldisulfonyl Azide	Gas Collected Ml. at S.T.P.	Sulfonamide[1] Isolated Product (Per Cent)
5.0	307, 310	43.8
9.7	304, 310	43.8
17.5	322, 328	41.0
29.8	327, 331	16.4
34.7	331, 341	13.7
100.0	371, 378	----

[1] To calculate the per cent yield, the sulfonamide isolated was considered to be a N,N'-bis(x-biphenylyl)-4,4'-biphenyldisulfonamide.

THERMAL DECOMPOSITIONS OF METHANESULFONYL AZIDE

Products of Decomposition of Methanesulfonyl Azide in Xylene

The only aliphatic sulfonyl azide studied was methanesulfonyl azide. It is the simplest organic sulfonyl azide and should therefore give a cleaner reaction than the larger aliphatic or aromatic sulfonyl azides.

Although methanesulfonyl azide was not found in the literature, it was easily prepared in 95 per cent yield by the method of Edmison (31) for the preparation of benzenesulfonyl azide. Ethanesulfonyl azide has

been prepared by Adams (1) using the same method. Ethanesulfonyl azide is reported to decompose at 128°C. and rapidly at 135°C.

The decomposition temperature for the work was chosen as 128°C. Decomposition is slow at 120°C. and very rapid at 135°C., which was the highest temperature tested. It is believed that the azide will decompose violently at 140°C. Therefore, it was decided that the temperature of 128°C. should give a sufficient rate and hold the possibility of an explosion to a minimum.

para-Xylene was chosen as the substrate since it has a boiling point of 138°C., since it was used in the earlier studies and since it will give only one product from a single azide attack, although there is a possibility of attack at four equivalent positions of the benzene ring.

Gas collections were made using the same apparatus as was used with the other azides. The gas was collected until no more was evolved for a 24-hour period. It was intended to run the reactions at concentrations of approximately 5, 10, 20, 30, 40 and 60 mole per cent methanesulfonyl azide. The amount of azide used, the gas collected and other data are shown in Table X.

The products of decomposition of methanesulfonyl azide in xylene were isolated by evaporating the xylene, dissolving the residue in 10 per cent sodium hydroxide, heating to 95°C., adding 2 grams of decolorizing charcoal, filtering and precipitating the product with concentrated hydrochloric acid. The products obtained from the reaction of methanesulfonyl azide in approximately 5, 10 and 20 mole per cent solutions (Table X) were white, but the products from the approximately 30, 40 and 60 mole per cent azide were a light tan color.

TABLE X

THERMAL DECOMPOSITION OF METHANESULFONYL AZIDE IN XYLENE

Azide Grams	Xylene Grams	Mole Per Cent Azide	Nitrogen Collected	Nitrogen Theoretical [1]	Per Cent Collected	Sulfonamide[2] Isolated Yield o: Product (Per Cen
1.5842	27.69	4.77	290.7	293.0	99.2	65.3
1.6759	29.24	4.78	305.1	309.9	98.5	61.7
1.5864	12.38	10.09	289.6	293.4	98.7	65.1
1.6207	12.64	10.10	297.0	299.7	99.1	63.8
1.7075	5.93	20.14	313.4	315.8	99.2	60.6
1.6671	5.85	19.99	303.4	308.3	98.4	58.4
1.5976	3.44	28.93	301.3	295.4	101.7	26.7
1.8038	3.87	29.00	341.8	333.6	102.4	30.3
1.4444	1.89	40.11	276.7	267.1	103.6	29.6
1.2987	1.72	38.54	253.1	240.2	105.4	24.6
1.5464	.94	60.79	301.7	286.0	105.5	23.6
1.8213	1.12	58.76	359.6	336.8	106.8	22.0

1/ This is calculated as the amount of nitrogen that would theoretically be given off if 2 of the 3 nitrogen atoms were released on heating.

2/ To calculate the per cent yield, the sulfonamide isolated was considered to be N-(p-xylyl)methanesulfonamide.

The standard for infrared comparison was prepared from one equivalent of methanesulfonyl chloride and two equivalents of 2,5-dimethylaniline which gave N-(p-xylyl)methanesulfonamide. One equivalent of the dimethylaniline was used as the hydrogen chloride acceptor. Ten per cent sodium hydroxide was added to the reaction products and the excess 2,5-dimethylaniline was extracted with ether. The sodium hydroxide solution was treated with decolorizing charcoal and filtered and the N-(p-xylyl)methanesulfonamide was precipitated by adding concentrated hydrochloric acid. It was filtered off, dried and recrystallized from ethanol. The melting point is 145°C. and no literature value was found. Nitrogen analyses were made in duplicate and the compound contained 6.97 and 6.95 per cent

nitrogen, compared to the theoretical value of 7.03 per cent nitrogen.

Infrared spectra were obtained from the products isolated from the reaction of methanesulfonyl azide at concentrations of 4.77, 10.10, 19.19, 28.93, 40.11 and 60.79 mole per cent, in xylene and the spectra obtained from the first four concentrations are shown in Figure 12. In Figure 13, the standard N-(p-xylyl)methanesulfonamide is compared with the isolated product obtained from the reaction of methanesulfonyl azide at the concentration of 10.10 mole per cent.

Products of Decomposition of Methanesulfonyl Azide Alone

Methanesulfonyl azide vaporizes to the cooler portion of the vessel when heated alone at 125°C. This difficulty was overcome to some extent by decomposing a sample in a 50-ml. boiling-flask connected to a reflux condenser. The flask and the condenser were immersed in a wax bath at 125°C. in such a way that the lower one-half inch of the outer condenser jacket was also in the hot wax. With water flowing through the condenser, this apparatus should have given a sharp temperature gradient and condensation would take place quickly and the distillate would return to the flask. It is not claimed that the results obtained are quantitative, but the qualitative results are useful.

A 5.0578-gram sample of methanesulfonyl azide decomposed at 125°C. in the manner described above gave a balck viscous liquid with no apparent condensate left in the condenser. This viscous liquid was dissolved and made to a volume of 250 ml. with distilled water. For the analyses, 50-ml. aliquots, equivalent to 1.0116 grams (8.35 milliequivents) of the original methanesulfonyl azide, were used. Two aliquots were titrated

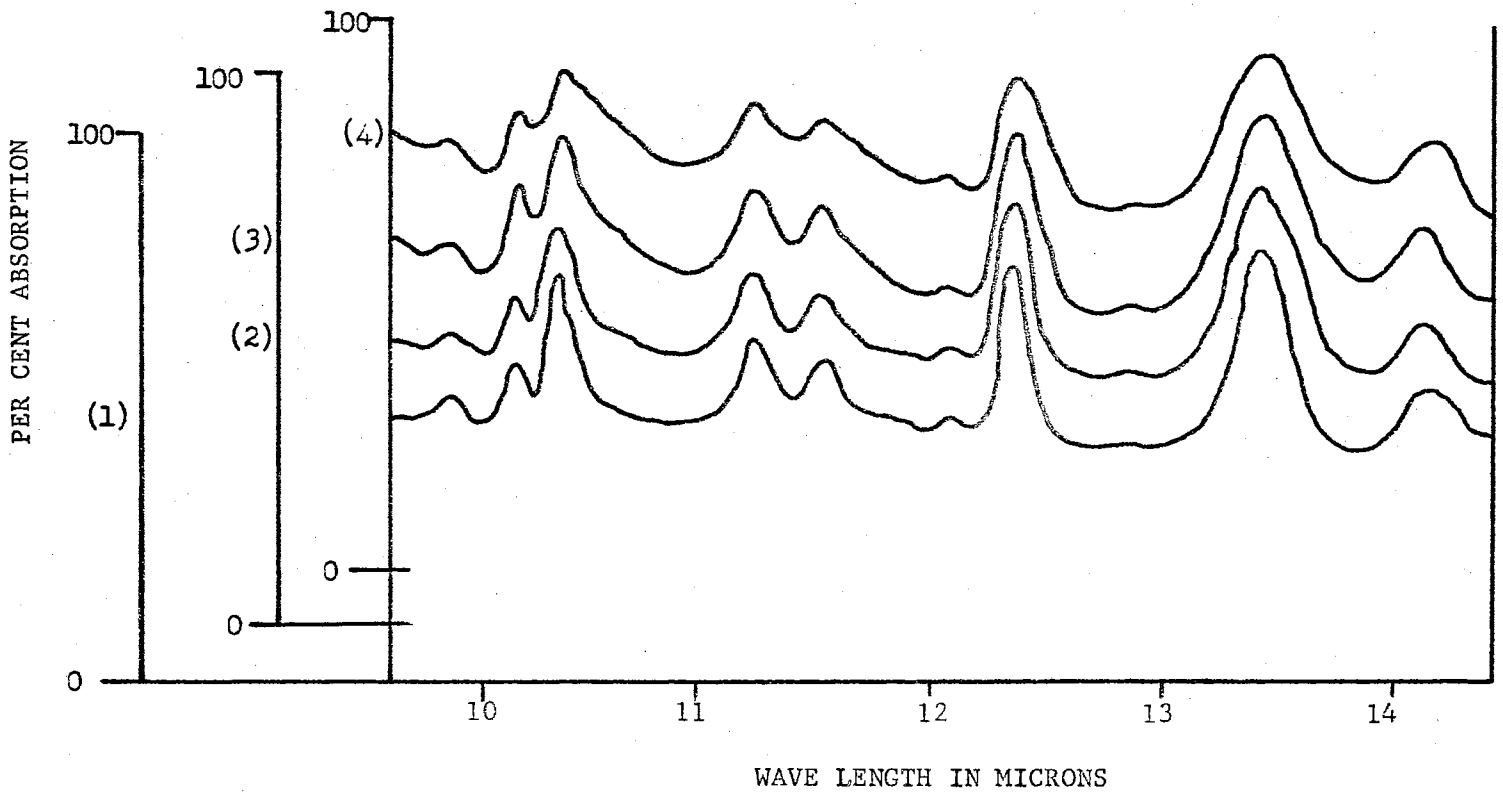


FIGURE 12: Absorption Curves of the Product from Decomposition of Methanesulfonyl Azide in Xylene at Azide Concentration of 4.8 (1), 10.1 (2), 19.2 (3) and 28.9 (4) Mole Per Cent.

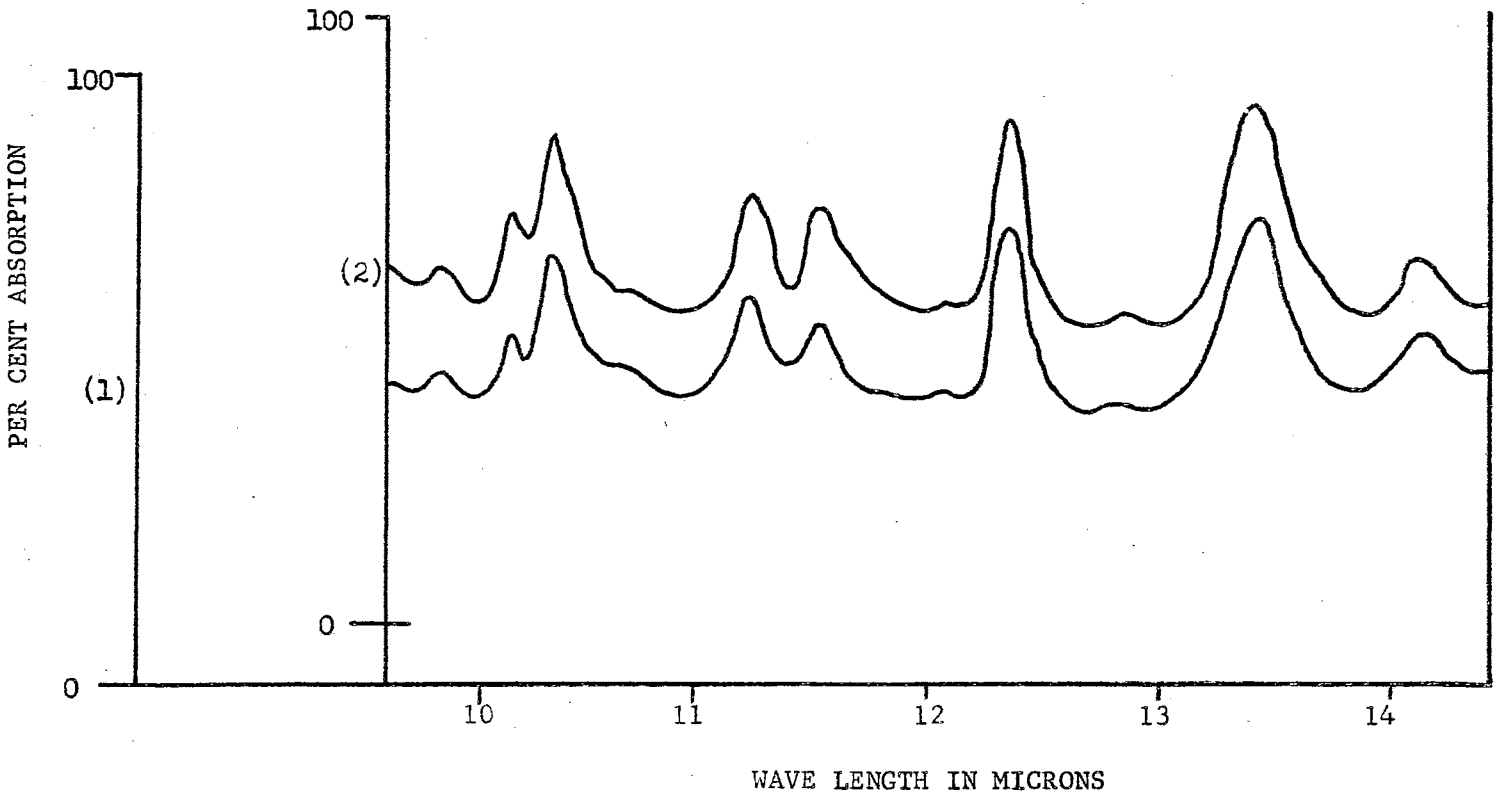


FIGURE 13: Absorption Curves of N-(para-Xylyl) Methanesulfonamide (1) and the Product from Decomposition of 10.1 Mole Per Cent Methanesulfonyl Azide in Xylene (2).

with standard base to a pH of 7 and then treated with 1.0116 grams of charcoal each to find the amount of product adsorbed per gram of charcoal. The acid found was 3.35 and 3.34 milliequivalents for the two samples and the amount of product adsorbed by the charcoal was 5.7 and 5.8 per cent, respectively. One of the filtrates was evaporated and a white residue was left. This residue was compared by infrared with sodium methanesulfonate and the spectra are shown in Figure 14. Standard sodium methanesulfonate was made by adding methanesulfonyl chloride to 10 per cent sodium hydroxide and allowing it to react until the chloride had disappeared. The solution was neutralized with hydrochloric acid and evaporated. Two other 50-ml. aliquots were treated with excess base and then distilled into standard acid. They were back-titrated with standard base and 1.44 and 1.42 milliequivalents of ammonia were found. The acid and ammonium salt found account for 57.1 per cent of the starting material and give an acid to ammonium salt ratio of almost five to two. It should again be mentioned that the above results may not be quantitative.

Kinetic Studies of the Decomposition of Methanesulfonyl Azide in Xylene

There are many ways to study the rate of reaction. They are all based on the rate of disappearance of reactants or the rate of formation of products. In the present example, there is not a known quantitative method for determining the amount of azide left or the amount of the substituted sulfonamide which has formed. Therefore, these studies were based on the amount of nitrogen evolved. It has been shown in the earlier work, using 15 mole per cent or less of an azide, that the nitrogen evolved is quantitatively equal to two-thirds of the theoretical nitrogen in the azide.

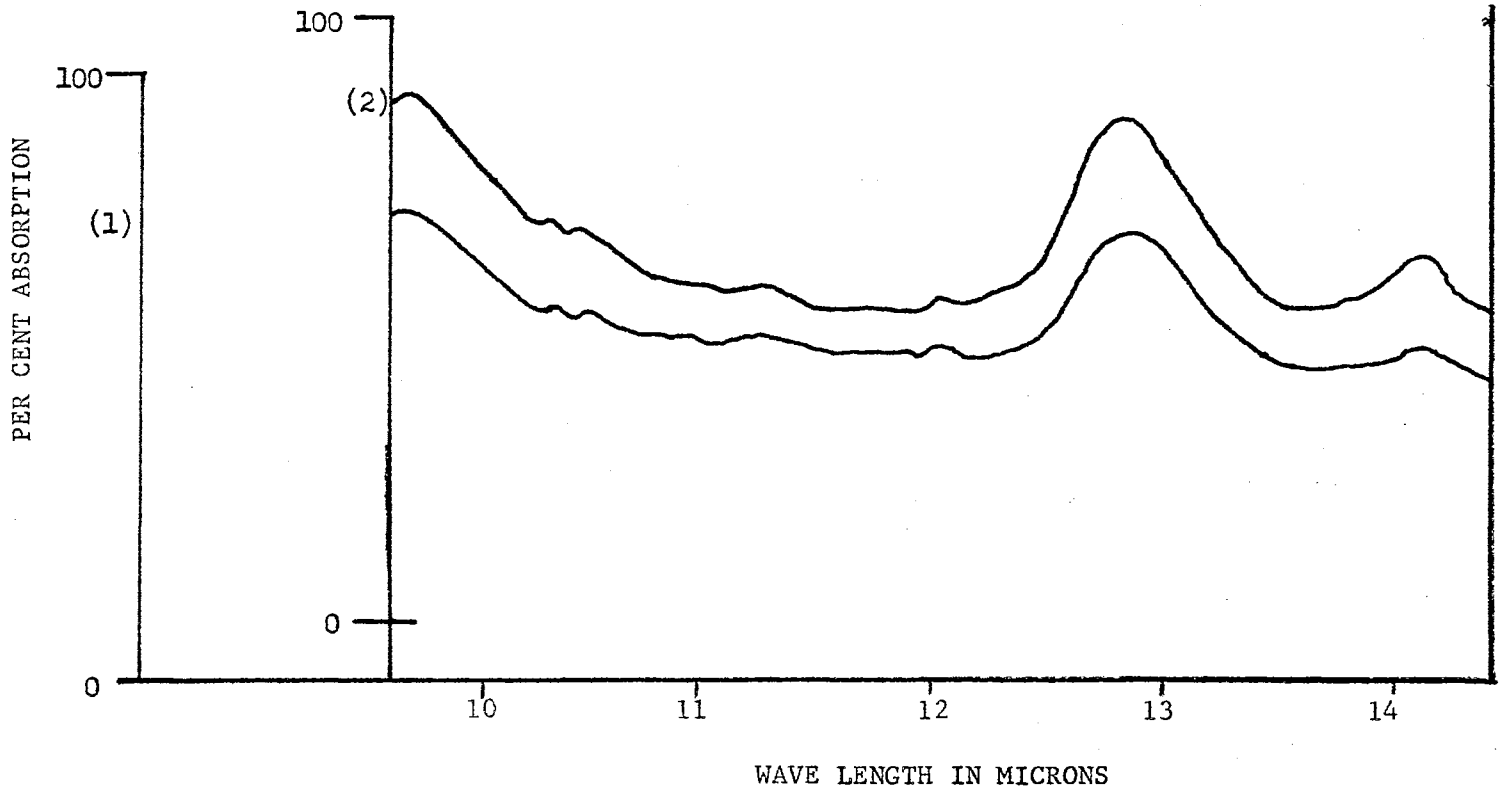


FIGURE 14: Absorption Curves of the Product from Methanesulfonyl Azide Decomposed Alone (1) and of Sodium Methanesulfonate (2).

It was decided to try to establish the order of reaction by two different methods. The first was by varying the concentration of methanesulfonyl azide in xylene and determining the rate of evolution of gas as a function of the concentration of azide used. The second was by decomposing an azide solution of known concentration in xylene and measuring the amount of gas evolved at successive intervals of time. The amount evolved in a given period of time would be proportional to the amount of azide remaining, if the reaction is first order.

The apparatus used consisted of a ground-glass side-arm test tube with a mercury-sealed stirrer. The side arm was connected to a gas burette which was connected to a leveling bulb. Boiling methyl Cellosolve was used to maintain a constant temperature of 123.4°C. in the test tube. The source of heat was a heating mantle.

In the first method, the methanesulfonyl azide and xylene were weighed into the reaction vessel. The reaction vessel was then placed in the methyl Cellosolve, initially at 30°C., and stirring was started. Heating was then started and some time before the initial measurement was made the side arm was connected to the gas burette. Eleven hours later, 22 hours after heating was started, the final reading was taken and the amount of gas collected was converted to S.T.P. Thus the gas collected over an 11-hour period was obtained. This procedure was followed for methanesulfonyl azide solutions with concentrations of 8.61, 4.71, 10.05 and 6.53 mole per cent. The results are shown in Table XI.

Comparison were made with trial one by considering the value of 39.42 ml. as 100 per cent. Then if 1.3238 grams of azide gave 39.42 ml. the 0.9158-gram sample (Trial 2) should give 26.97 ml. but only 26.04 ml. were

found; this is 96.6 per cent of 26.97 ml. and is given in column four. The other two trials were similarly compared with trial one as the standard. The data indicate the degree of conformance to first order kinetics but the rate constant cannot be calculated by this method.

TABLE XI

GAS COLLECTED FROM THERMAL DECOMPOSITION OF METHANE-SULFONYL AZIDE IN XYLENE DURING ELEVEN HOURS

Trial	Weight of Azide, Grams	Mole Per Cent Azide	Gas Collected ml. S.T.P.	Comparison with Trial 1 (Per Cent)
1	1.3238	8.61	39.42	100.0
2	.9158	4.71	26.04	96.6
3	1.7812	10.05	52.86	99.6
4	1.2110	6.53	36.39	100.9

The same apparatus was used with the second method. The methyl Cellosolve was brought to boiling. The reaction vessel, containing a weighed amount of nitrogen-saturated xylene, was immersed into the methyl Cellosolve to such a depth that all the xylene was covered. The side arm was connected to the gas burette. The methanesulfonyl azide was heated to 80°C. and added to the xylene in the reaction vessel. The stirrer was set in place and stirring was started. The system was then closed by making the mercury seal on the stirrer. Readings were taken from the gas burette every four hours for the first 16 hours and then every eight hours thereafter until the reaction was stopped. The volume of gas evolved was converted to S.T.P. The results obtained from Trial I using 1.5001 grams of methanesulfonyl azide, a 10.20 mole per cent solution, are shown in Table XII. A graph of these data is shown in

Figure 15. The results obtained from Trial II using 1.4072 grams of methanesulfonyl azide, a 9.13 mole per cent solution, are also shown in Table XII. A graph of these data is shown in Figure 16.

TABLE XII

GAS COLLECTED FROM THERMAL DECOMPOSITION OF METHANESULFONYL AZIDE IN XYLENE DURING FORTY-EIGHT HOURS

Trial I		Trial II	
1.5001 Grams of Methanesulfonyl Azide		1.4072 Grams of Methanesulfonyl Azide	
Time, Hours	Volume N_2 ml. at S.T.P.	Time Hours	Volume N_2 ml. at S.T.P.
4	23.4	4	23.8
8	44.2	8	43.7
12	65.0	12	62.7
16	84.4	16	80.1
24	116.2	24	111.1
32	139.6	32	132.7
40	158.8	40	151.4
48	174.2	48	164.6

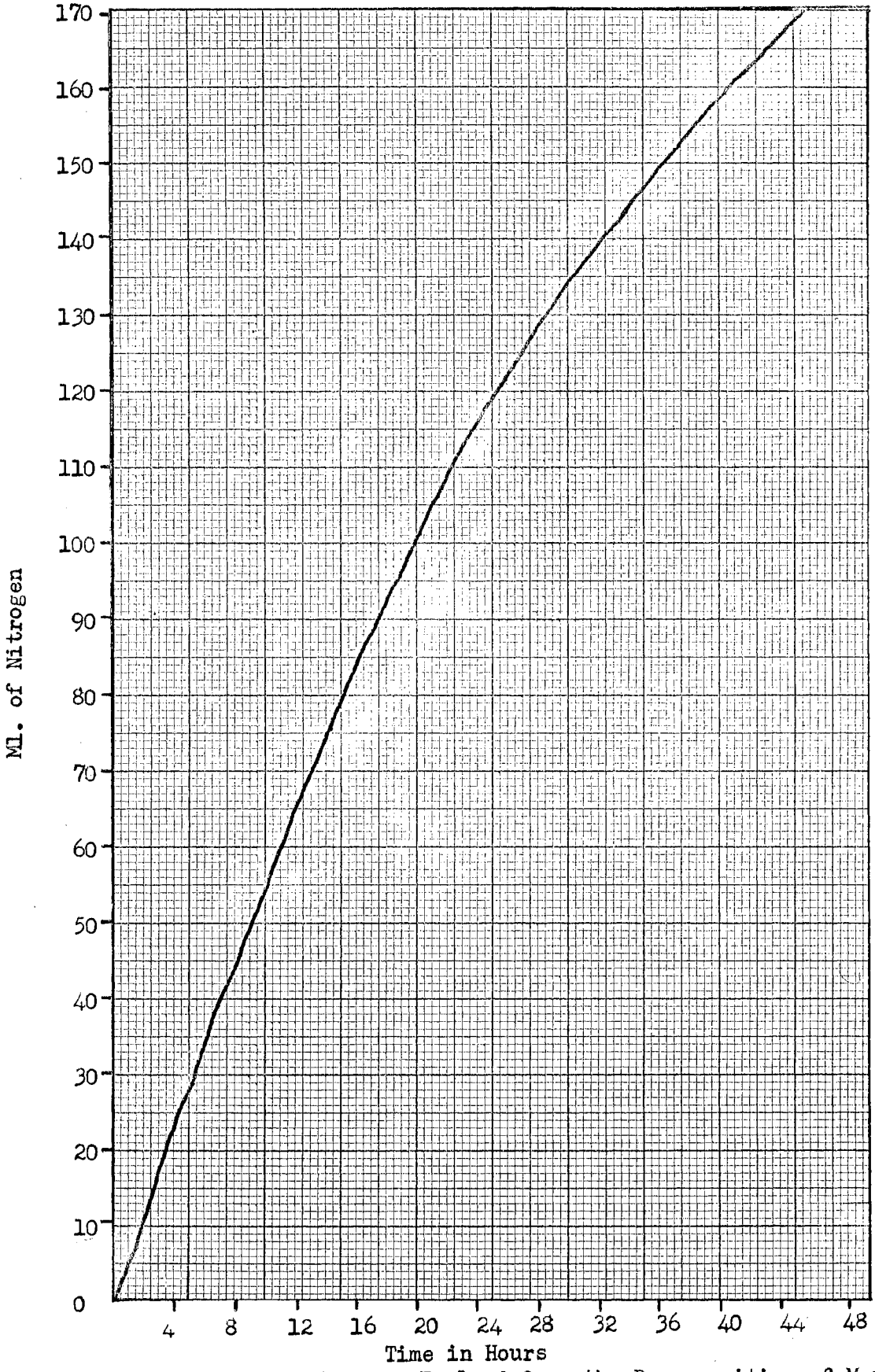


FIGURE 15: Ml. of Nitrogen Evolved from the Decomposition of Methanesulfonyl Azide in Xylene Versus Time in Hours.

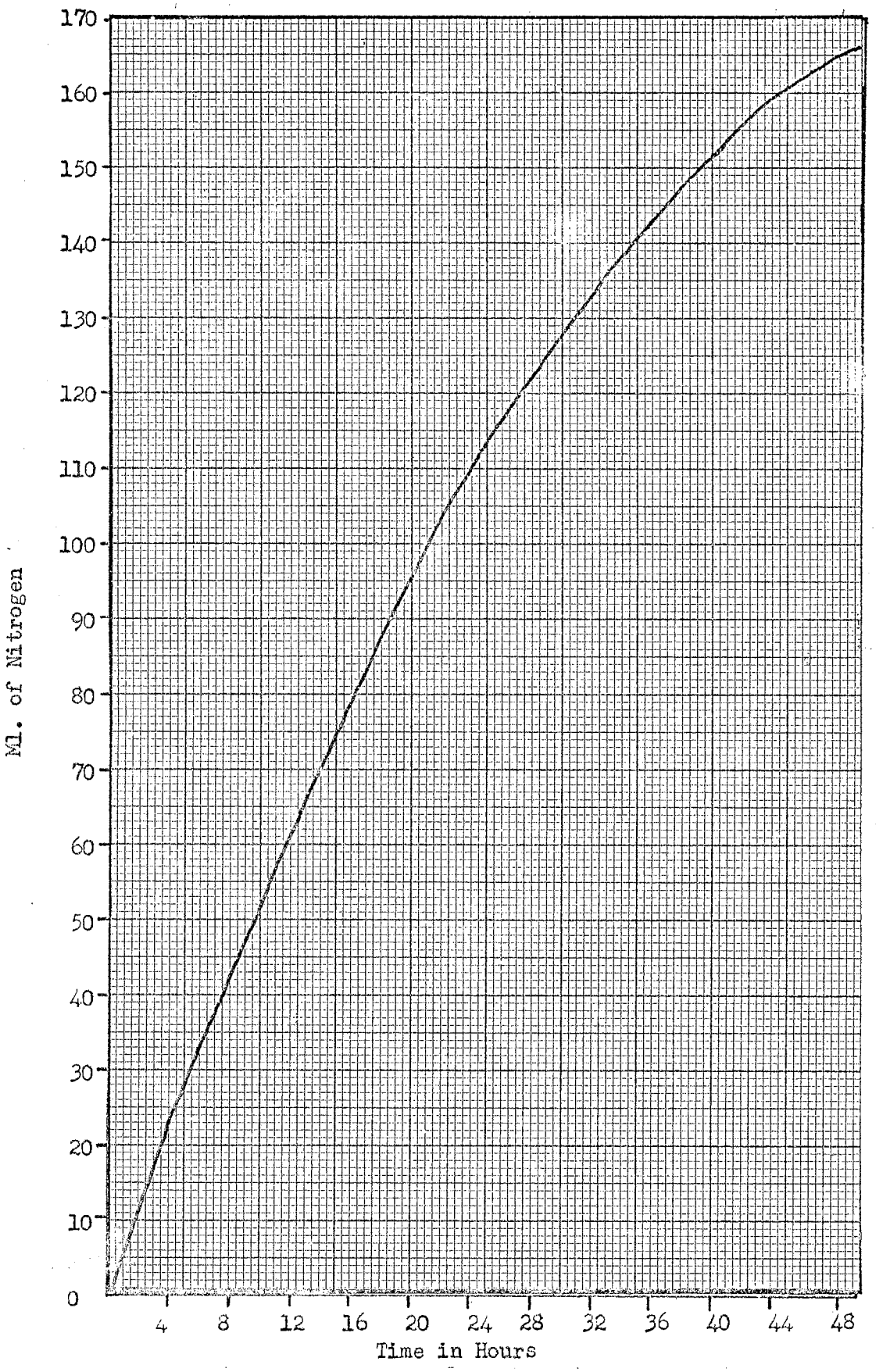


FIGURE 16: Ml. of Nitrogen Evolved from the Decomposition of Methanesulfonyl Azide in Xylene Versus Time in Hours.

DISCUSSION AND CONCLUSION

The 1,4-benzenedisulfonyl azide was chosen because it would give a more linear and presumably more useful product than the more readily obtained 1,3-benzenedisulfonyl azide. The percentage yields for the preparation of potassium 1,4-benzenedisulfonate may seem somewhat low. If one considers the number of steps in the procedure and the fact that the four position of the benzenesulfonic acid is already deactivated, the yields do not seem so low. One disadvantage of preparing 1,4-benzenedisulfonyl azide by this method is that there is not a suitable intermediate that can be identified until the 1,4-benzenedisulfonyl chloride is prepared. Once an aromatic disulfonyl chloride is prepared, it can be converted in good yields (approximately 95 per cent) to the disulfonyl azide by reaction with sodium azide. The azide may be purified by recrystallization from ethanol. However, the larger molecular weight aromatic disulfonyl azides (e.g. 4,4'-biphenyldisulfonyl azide) are not very soluble in common organic solvents.

Products of Thermal Decomposition of 1,4-Benzenedisulfonyl Azide

Aromatic disulfonyl azides can be decomposed smoothly, with or without a substrate, at 120°C. However, in order to get a sufficient rate of decomposition, the 4,4'-biphenyldisulfonyl azide and the 1,5-naphthalenedisulfonyl azide should be heated at 135°C.

When the concentration of 1,4-benzenedisulfonyl azide is 5.0, 9.7 or 17.5 mole per cent and the substrate is biphenyl, the product isolated is a mixture of N,N'-bis(4-biphenylyl)-1,4-benzenedisulfonamide and N,N'-bis(2-biphenylyl)-1,4-benzenedisulfonamide. That these were the reaction products was confirmed by the infrared spectra shown in Figures 2 and 3. At these concentrations, the amount of gas evolved was 310 ml. This value is the average of the results shown in Table V for concentrations of 5.0, 9.7 and 17.5 mole per cent azide.

The yield of isolated products at these concentrations was almost constant although somewhat lower than might be expected. The yields were 64 to 67 per cent as shown in Table V. The value of 310 ml. is four-sixths of the total nitrogen present and thus would leave enough nitrogen to form a 100 per cent yield of disulfonamide.

Either the disulfonamide did not form in this amount or it was not all isolated by the method used; the dark color of the reaction mixture is evidence of side reactions. The reaction evidently proceeds by the same predominent mechanism at all of these concentrations.

When 1,4-benzenedisulfonyl azide was decomposed alone at 120°C. open to the air, a black viscous liquid was obtained. When it was decomposed under the same conditions, but opened to the air through a calcium chloride drying tube, a black powdery solid was obtained. If the calcium chloride tube was removed after decomposition, the black solid became the black viscous liquid. This indicated a very hydroscopic material. This property along with the color made it impossible to obtain infrared data. Considerable heat was given off when the black solid was dissolved in water. Less heat was given off when the black viscous liquid was dissolved in water.

The products obtained from the decomposition of 2.0000 grams of 1,4-benzenedisulfonyl azide in 50 ml. of water gave off enough heat for the tube to feel warm to the touch. The solution obtained was very acidic (pH less than 1) and no insoluble material was left when the solution was filtered. The odor of ammonia was noted when excess sodium hydroxide was added. These facts would mean that substituted disulfonamides are not formed by self attack since they are insoluble in water and are stable to base.

The labile nitrogen was 388 ml. (Table V) which is halfway between the theoretical 310 ml. for disulfonamide formation and the total nitrogen of 466 ml. To state this differently, five-sixths of the total theorectical nitrogen was evolved. The remaining (residual) nitrogen was determined by Kjeldahl nitrogen analysis and found to be 72 ml. Of these 72 ml., 55 ml. were freed in the form of ammonia by adding excess sodium hydroxide. The remaining nitrogen might possibly be in the form of 1,4-benzenedisulfonamide, which is slightly soluble in water, but none of this compound was isolated. It could also be combined in such compounds as the unknown dye.

The analyses for disulfonic acid and monoammonium salt together accounted for 73.4 per cent of the residual solid material present. That sodium 1,4-benzenedisulfonate was formed by hydrolysis and neutralization with sodium hydroxide is shown by the infrared spectra in Figure 5. Thus the greater portion of the 1,4-benzenedisulfonyl azide must be cleaved at the sulfur-nitrogen bond when the azide is decomposed alone. This mechanism could also be taking place when there is no large excess of a substrate present.

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Proposed Mechanism of Reaction at Lower Concentrations of Aromatic Disulfonyl-Azide

There is no doubt, in the opinion of the author, that the mechanism at lower azide concentrations is like the mechanism conceived by Dermer and Edmison (29) for the reactions of benzenesulfonyl azide. The azide concentration used in their work was 5-10 mole per cent of benzenesulfonyl azide. The resulting mechanism for low concentrations of disulfonyl azides would follow as:

1. $N_3O_2SArSO_2N_3 \longrightarrow N_3O_2SArSO_2N: + N_2$
2. $N_3O_2SArSO_2N: + Ar'H \longrightarrow N_3O_2SArSO_2NHAr'$
3. $Ar'NHO_2SArSO_2N_3 \longrightarrow Ar'NHO_2SArSO_2N: + N_2$
4. $Ar'NHO_2SArSO_2N: + Ar'H \longrightarrow Ar(SO_2NHAr')_2$

None of the present experimental results contradict this proposed mechanism; however, it has not been definitely proven.

Proposed Mechanism of Reaction For Organic Sulfonyl Azides Decomposed Alone

It has been very difficult to devise a mechanism that would fit the experimental data and not contradict any of the known properties of the type compounds that might be formed. The greatest difficulty was encountered in explaining how the azide nitrogen was reduced to ammonia. There is no literature precedent of this for decomposition of organic azides and only one instance (to the authors knowledge) that might be considered of the same type. Backer (4) found that bis(methylsulfonyl)isonitrosomethane decomposed on standing at room temperature and evolved carbon dioxide with the formation (among other things) of some ammonium methanesulfonate. However, he did not suggest a mechanism.

The postulated mechanism for the thermal decomposition of a disulfonyl azide at high concentrations is as follows:

1. $RSO_2N_3 \longrightarrow RSO_2N: + N_2$

2. $RSO_2N: + N\equiv\overset{+}{N}-\overset{-}{N}-SO_2R \longrightarrow RSO_2-\overset{-}{N}-\overset{\overset{N}{\equiv}}{\underset{|}{N+}}-SO_2R$

3. $RSO_2\overset{-}{N}-\overset{\overset{N}{\equiv}}{\underset{|}{N+}}-SO_2R \longrightarrow R\overset{+}{S}O_2 + R\overset{-}{S}O_2 + 2\,N_2$

4. $R\overset{-}{S}O_2 \longrightarrow RSO_2^-$

5. $RSO_2^- + R\overset{+}{S}O_2 \longrightarrow R-\overset{\overset{O}{\|}}{S}-O-\overset{\overset{O}{\|}}{S}-R$ (O)

6. $RSO_2^- + RSO_2N: \longrightarrow R-\overset{\overset{O}{\|}}{S}-O-\overset{-}{N}-\overset{\overset{O}{\|}}{S}-R$ (O)

7. $R-\overset{\overset{O}{\|}}{S}-O-\overset{-}{N}-\overset{\overset{O}{\|}}{S}-R + R-\overset{+}{S}O_2 \longrightarrow R-\overset{\overset{O}{\|}}{S}-O-N(SO_2R)_2$ (O)

8. $R-S-O-N(SO_2R)_2 + 3HOH \longrightarrow RSO_2H + RSO_3H + RSO_3NH_4$

9. $R-\overset{\overset{O}{\|}}{S}-O-\overset{\overset{O}{\|}}{S}-R + HOH \longrightarrow RSO_2H + RSO_3H$ (O)

10. $RSO_2H + \text{air} \longrightarrow RSO_3H$

R may be a methyl group, a phenylene-4-sulfonyl azide group, a phenylene 3-sulfonyl azide or a biphenylene-4'-sulfonyl azide. The second sulfonyl azide group of R, in the latter three cases, would be capable of undergoing the same reactions; e.g. either decomposing and attacking another

sulfonyl azide or being attacked by another fragment, formed in step one, and thus R in these cases would be a chain-carrying intermediate.

In step 2 there is a possibility of the four nitrogens forming a linear linkage rather than the one postulated. This would be formed by the reaction of the radical from step 1 with the canonical form of the sulfonyl azide which has a negative charge on the end nitrogen atom. The one written is more likely because of the pull of electrons by the sulfonyl group of the azide, so that the electrons should be more localized around the nitrogen next to the sulfonyl group. Whichever one is chosen would give the products postulated in step 3.

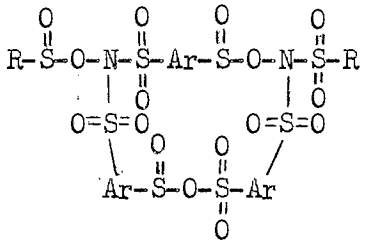
Step 4 must be fast to avoid the formation of a disulfone which apparently is not formed. This would be feasible since the ion with the negative charge on the sulfur would not be as stable as one with the charge localized on an oxygen atom, because of the larger electron attraction of the oxygen atoms. Sulfinic acids were never isolated or shown to be present in any of the experimental work so step 10 would have to be an easy oxidation. Sidgwick (50) states that the sulfinic acids are unstable in air and are oxidized by air to the sulfonic acids.

There was no experimental evidence that contradicted this mechanism and it readily explains the products which were isolated, after hydrolysis of the black material which resulted from the decomposition of 1,4-benzenedisulfonyl azide.

Intermediate Obtained from the Thermal Decomposition of 1,4-Benzenedisulfonyl Azide Alone.

With the postulated mechanism, it is quite easy to draw an intermediate that will give the 3 free acid groups to 1 ammonium salt group which are

obtained from the decomposition of 1,4-benzenedisulfonyl azide. This intermediate could have the following structure



R is the chain-carrying fragment and Ar is the 1,4-phenylene group. Upon hydrolysis of this intermediate with four molecules of water, and air oxidation of the resulting sulfinic acid, it will give three free acid groups for each ammonium salt group. As can be seen from the formula, this is only composed of a molecule formed by a combination of steps 5 and 7 of the propsed mechanism.

Since the reaction is a pyrolysis it might be supposed that it proceeds by a radical mechanism. If this were true, disulfones should be formed by the combination of two arene sulfonyl radicals ($ArSO_2\cdot$), which would have to be formed if a radical mechanism was postulated. As stated earlier, the disulfones are water-insoluble and were not found after decomposition of the azide. This alone is enough to rule out a radical mechanism for all but the initial steps in the decomposition.

Interpretations From Amount of Gas Collected

From the amounts of gas collected, it can be seen that somewhere between azide concentrations of 17.5 and one of 29.8 mole per cent the reaction begins to go by the mechanism of high concentrations. This

could mean that there is not a large enough excess of biphenyl present or at the higher concentration of azide the electron-deficient nitrogen prefers to attack another electron-rich azide group in preference to a aromatic nucleus.

The latter explanation could also be used to explain why further substitution on the N-para tolylbenzenesulfonamide did not occur and why no sulfonamides were isolated by Edmison (31) and Heacock (38) when they decomposed benzenesulfonyl azide in aromatic compounds containing meta-directing groups.

Comparison of 1,3-Benzenedisulfonyl Azide with 1,4-Benzenedisulfonyl Azide

The results from thermal decompositions of 1,3-benzenedisulfonyl azide are very similar to the results which were obtained with 1,4-benzenedisulfonyl azide. The total nitrogen found (Table I) in 1,3-benzenedisulfonyl azide was closer to the theoretical value than the total nitrogen found in 1,4-benzenedisulfonyl azide. On the average, there were 30 ml. more labile nitrogen obtained from the 1,3-benzenedisulfonyl azide. The decomposition temperature (approximately 100°C.) is about the same even though there is 53°C. difference in the melting points of the two diazides. The 1,4-benzenedisulfonyl azide decomposes violently just above its melting point.

The infrared spectra (Figures 4, 5, and 6) show that the isolated products of decomposition of 1,3-benzenedisulfonyl azide are the same as those from the 1,4-benzenedisulfonyl azide except for the fact that the former contain 1,3-disubstituted benzene rings. Thus 1,3-disbstituted disulfonamides are formed instead of 1,4-disubstituted disulfonamides and 1,3-benzenedisulfonic acid instead of the 1,4-benzenedisulfonic acid. The yields of products were just slightly lower for the 1,3-benzenedisulfonyl azide.

One large difference was the amount of material adsorbed by 1 gram of charcoal after dissolving the products of the azide decomposition in water. It was about 5 times as great for 1,3-benzenedisulfonyl azide. No interpretation of this is possible at present.

The analyses for disulfonic acid and monoammonium salt accounts for 67 per cent of the solid material present. The amount of ammonia formed after hydrolysis of products from azide decompositions, was about one-third as great for the 1,3-benzenedisulfonyl azide as for the 1,4-benzenedisulfonyl azide. This could be explained by the positions of the sulfonyl groups. With the disulfonyl groups in the one and three positions, more of the reaction could proceed by step 5 (page 64) whereas when the groups are in the one and four positions, more of it proceeds by step 7. From the amounts of gas collected during the reaction at various concentrations of 1,3-benzenedisulfonyl azide in biphenyl (Table VII) it is evident that at 27.9 mole per cent and above some of the reaction proceeds by the mechanism which occurrs when azides are decomposed alone. This is also the concentration at which the mechanism change occurrs when decomposing the 1,4-benzenedisulfonyl azide.

An intermediate for the 1,3-benzenedisulfonyl azide may be pictured as consisting of the products formed in step 5 and 7 in a ratio of 3.15 to 1. This intermediate on hydrolysis would give the experimentally found ratio of free acid groups to ammonium salt group of 8.30 to 1. To obtain this ratio would require a very large intermediate, i.e., very high molecular weight.

Comments About the 4,4'-Biphenyldisulfonyl Azide

The results of 4,4'-biphenyldisulfonyl azide decompositons are comparable to the results obtained with the other azides but a few differences should be noted. The decomposition temperature of 135°C. gives a somewhat slower rate of decomposition than the rate obtained with either the 1,3- or the 1,4-benzenedisulfonyl azide decomposed at 120°C. The amount of gas collected is comparable with that from the 1,4-benzenedisulfonyl azide but the yield of isolated products is lower (Table IX). The lower yields obtained could be due to the lower solubility of the products in 10 per cent sodium hydroxide and the formation of colloidal precipitates, even at the lower azide concentrations, which were difficult to isolate by filtration or by other means.

The infrared spectra (Figure 9) show that the same product was isolated after decompositions of the 4,4'-biphenyldisulfonyl azide in various concentrations with biphenyl as the substrate. The infrared spectra (Figure 11) show that the 4,4'-biphenyldisulfonic acid was isolated when the azide was decomposed alone. The infrared spectra comparing the standards with isolated products (Figure 10) do not exactly match but are very close. Only two compounds, out of the numerous isomers, were prepared as standards and used for the comparison. The author has no doubt that a matching spectrum of the disubstituted disulfonamides could be made either by using the right proportion of each of the two standards already prepared, N,N'-bis(2-biphenylyl)-4,4'-biphenyldisulfonamide and N,N'-bis(4-biphenylyl)-4,4'-biphenyldisulfonamide or it might be that a reaction between a mixture of the 2- and 4-amino biphenyl with the 4,4'-biphenyldisulfonyl chloride would give the proper standard for comparison.

Products of Thermal Decomposition and Proposed Mechanism of Reaction at Low Concentrations of Methanesulfonyl Azide

Methanesulfonyl azide is easily prepared, but being a liquid, it is somewhat difficult to purify. All experimental results indicate the method used to purify it was satisfactory and a relatively pure compound was obtained.

The reactions of methanesulfonyl azide in xylene were cleaner than the reactions of the other azides and xylene. The solutions, after azide decompositon, were a light tan color at concentrations below 30 mole per cent and above 30 mole per cent the solutions were brown in color. The percentage yields were about the same at the lower conentrations, but at concentrations of 30 mole per cent and higher they were considerably lower. The products isolated were white except at the higher concentrations and these products were a light tan. However, infrared spectra (Figure 12) show the isolated products from the several runs to be all the same. Figure 13 shows that the spectrum of the product isolated after decomposition of the 10.10 mole per cent methanesulfonyl azide solution is the same as the N-(p-tolyl)methanesulfonyl chloride.

The mechanism of the reaction of methanesulfonyl azide in xylene may be conceived as follows:

1. $CH_3SO_2N_3 \longrightarrow CH_3SO_2N: + N_2$

2. $CH_3SO_2N: + ArH \longrightarrow CH_3SO_2NHAr$

The reaction apparently proceeds by this mechanism at 20 mole per cent and lower azide concentrations. If the mechanisms at higher concentration (page 64) is operating, in addition to the one just postulated, at the 30 mole per cent azide concentration, or higher, it is doing so to a

limited extent. The gas collections show (Table X) that the amount of gas evolved, at an azide concentration of 20 mole per cent or less is less than 100 per cent of the theoretical value that could be evolved according to the sample substitution mechanism. However, at the 30 mole per cent azide concentration, or higher, the amount of gas evolved is over 100 per cent so both mechanisms could be operating.

The infrared spectra (Figure 14) show that methanesulfonic acid resulted when the azide was decomposed alone and the products of the reaction were dissolved in water. At this concentration, it is believed that the mechanism postulated for the higher concentration is operating.

Kinetic Studies of Methanesulfonyl Azide Decomposed in Xylene

In the kinetic study where the concentration of methanesulfonyl azide was varied from 6 to 10 mole per cent, it was shown, within experimental error, that the amount of gas released in a fixed period of time, 11 hours, was directly porportional to the concentration of methanesulfonyl azide with a maximum negative deviation of 3.4 per cent and a positive deviation of .9 per cent. These deviations are based upon the first experiment and would be different if another of the experiments was assigned a value of 100. However, the absolute deviation would not change.

More significant information was obtained from the kinetic study where the gas was collected from the start of decomposition until 62.8 per cent of the azide has decomposed. If the reaction is first order, the rate constant, k, will be constant when calculated from the equation $kt = \ln (a/a-x)$ where t is the time in seconds, a is the initial amount present and a-x is the amount remaining (32).

In Table XIII are shown the data for calculating the rate constant and the rate constant found using the above equation.

TABLE XIII

RATE CONSTANTS FOR THE THERMAL DECOMPOSITIONS OF METHANESULFONYL AZIDE IN XYLENE

Trial I

1.5001 Grams of Methanesulfonyl Azide
(a = 277.4 ml.)

Time Sec.	Ml. of N_2, S.T.P. (x)	(a-x) Ml.	k x 10^6 $Sec.^{-1}$
14,400	23.4	254.0	6.4
28,800	44.2	232.2	6.0
43,200	65.0	212.4	6.2
57,600	84.4	193.0	6.3
86,400	116.2	161.2	6.3
115,200	139.6	137.8	6.1
144,000	158.8	118.6	5.9
172,800	174.2	103.2	5.7

Trial II

1.4072 Grams of Methanesulfonyl Azide
(a = 260.2 ml.)

Time Sec.	Ml. of N_2, S.T.P. (x)	(a-x) Ml.	k x 10^6 $Sec.^{-1}$
14,400	23.8	236.4	6.7
28,800	43.7	216.5	6.4
43,200	62.7	197.5	6.4
57,600	80.1	180.1	6.4
86,400	111.1	149.1	6.5
115,200	132.7	127.5	6.2
144,000	151.4	108.8	6.1
172,800	164.6	95.6	5.9

The average rate constant k, is 6.1 x 10^{-6} $sec.^{-1}$ for Trial I and 6.3 x 10^{-6} $sec.^{-1}$ for Trial II. The average k values are consistent enough to say that the reaction shows first order kinetics. The individual

k values deviated from the average k a maximum of 6.6 per cent on Trial I and 6.3 per cent on Trial II.

SUMMARY

Organic sulfonyl azides were prepared by reacting the sulfonic acids with phosphorus pentachloride to convert them to the sulfonyl chlorides. The sulfonyl chlorides were reacted with sodium azide to convert them to the sulfonyl azides. Azides prepared by using this method were 1,3-benzenedisulfonyl azide, 1,4-benzenedisulfonyl azide, 4,4'-biphenyldisulfonyl azide and 1,5-naphthalenedisulfonyl azide. Sulfonyl azides which were prepared from the sulfonyl chlorides as starting materials were benzenesulfonyl azide, 4-nitrobenzenesulfonyl azide and methanesulfonyl azide.

The disulfonyl azides were thermally decomposed individually at various concentrations (3-40 mole per cent azide) with toluene, xylene, naphthalene, biphenyl, 1,4-dichlorobenzene and 1,2,4,5-tetrachlorobenzene, individually, as substrates.

The nitrogen which was evolved in the decomposition of the disulfonyl azides (except from 1,5-naphthalenedisulfonyl azide) in biphenyl was measured. At azide concentrations of less than 15 mole per cent, approximately two-thirds of the theoretical nitrogen was evolved. At azide concentrations greater than 25 mole per cent, the nitrogen evolved was greater than two-thirds of the theoretical nitrogen.

Products were isolated by a purification procedure described in the experimental section. In all cases the product yields were smaller and

the products were darker as the azide concentration was increased. Infrared spectra were obtained on these products and the spectra were found to be qualitatively the same. Standard compounds were prepared in each case by reacting 2-amionbiphenyl and 4-aminobiphenyl respectively with the proper disulfonyl chloride. These standards were isolated by the same purification procedure as that which was used with the products of azide decomposition. By changing the ratio of the standards, matching infrared spectra were obtained from the products isolated from the decomposition of the 1,4- and 1,3-benzenedisulfonyl azides. Similar spectra were obtained with products from the decomposition of 4,4'-biphenyldisulfonyl azide and the corresponding standards.

The disulfonyl azides were thermally decomposed alone and the resulting products were dissolved in water. The products identified in these solutions were the disulfonic acids and the monoammonium salt of the disulfonic acids. The compounds were identified by comparing their infrared spectra with the infrared spectra of the disulfonates that had been made by neutralizing the disulfonic acids. These two compounds were present in concentrations that accounted for 65-72 per cent of the initial disulfonyl azide.

Methanesulfonyl azide was thermally decomposed in xylene at azide concentrations from 4.8 to 60.0 mole per cent. The yield of isolated product was 22.0 to 65.3 per cent and was shown by infrared spectra to be the N-(p-xylyl)methanesulfonamide. The gas collections showed that a different mechanism started operating at an azide concentration above 20 mole per cent and became the predominant course of the reaction at high concentrations. Vaporization of the azide was noted at concentrations

of 40 and 60 mole per cent. Therefore, quantitative analyses of products from the decomposition of the azide alone were not possible. However, the methanesulfonic acid and ammonium methane sulfonate accounted for 57 per cent of the starting material. The thermal decomposition of 10 mole per cent methanesulfonyl azide at 123°C. in xylene, exhibited first order kinetics and the rate constant was calculated.

SUGGESTIONS FOR FUTURE WORK

Future work with the disulfonyl azides should include careful qualitative and quantitative analyses of all reaction products. This research has shown that the larger portion of the product at low concentrations of azide is N-substituted sulfonamides and for the azide alone it is sulfonic acid (and ammonium salt), but there was not a single experiment that accounted for all of the starting azide. In reactions between an azide and a substrate where the mechanism of high concentration (more than two-thirds of nitrogen liberated per mole) is operating, the amount of acid and ammonium salt formed should be determined.

Future work that could help prove the postulated mechanism at high concentration should include an analysis for sulfinic acid. To show this, the azide should be decomposed in an inert atmosphere. After decomposition, the material could be titrated with an oxidizing agent like iodine in carbon tetrachloride.

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